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I. Physical & Chemical Properties Division (838)

W. Mickey Haynes, Acting Chief
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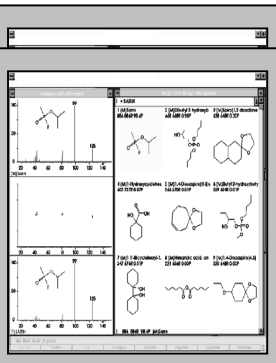


Physical & Chemical Properties

R. Huie, Acting Chief

- Fluid Science
- Experimental Kinetics & Thermodynamics
- Chemical Reference Data & Modeling
- Computational Chemistry
- Experimental Properties of Fluids
- Theory & Modeling of Fluids
- Cryogenic Technologies

A. Division Overview

Mission

The Physical and Chemical Properties Division serves as the Nation's reference laboratory for measurements, standards, data, and models in the areas of thermophysics, thermochemistry, and chemical kinetics. The Division focuses primarily on:

- thermochemical and thermophysical properties of gases, liquids, and solids, both as pure materials and as mixtures;
- rates and mechanisms of chemical reactions in the gas and liquid phases; and
- fluid-based physical processes and systems, including separations and low-temperature refrigeration and heat transfer.

The Division outputs include technical reports, Standard Reference Data, internet-based databases, calibrations, and Standard Reference Materials.

In order to carry out this Mission, the Division:

- develops, maintains, and utilizes advanced experimental tools and applies these to problems of scientific and industrial importance;
- compiles, evaluates, correlates, and interprets experimental data;
- develops and evaluates new theories, models, estimation methods, and computational algorithms;
- develops new dissemination mechanisms while maintaining a strong publication record in traditional media;
- carries out research leading to engineering data and models for advanced technologies; and

provides standards and services for fluid flow under cryogenic conditions.

Programs

The Physical and Chemical Properties Division is organized into seven groups:

- Fluid Science;
- Experimental Kinetics and Thermodynamics;
- Chemical Reference Data and Modeling;
- Computational Chemistry;
- Experimental Properties of Fluids;
- Theory and Modeling of Fluids, and
- Cryogenic Technologies.

The last three Groups are located in Boulder, CO, as are two Projects, Properties for Process Separations and Membrane Science and Technology. The rest of the Division is located in Gaithersburg, MD. These Groups and Projects are engaged in a number of research activities, which arise from several focus areas that cut across Group/Project boundaries. These focus areas are discussed below, followed by selected Technical Reports from these activities.

Basic Reference Data

Industry is demanding reliable and accessible reference data on the physical and chemical properties of a wide variety of compounds at an increasing rate. These data are required in the development of models for process design, energy efficiency, and in the evaluation of possible environmental impacts. Basic reference data are also critical to the transportation and storage of fluids and in custody transfer.

The development of databases for use in industry and academia is a fundamental task of all the focus

areas within the Division. Thus, many of the Technical Reports pertain both to Basic Reference Data and to a specific technical focus area. The notable exception to this is the NIST Chemical WebBook, which is a data dissemination tool that is designed ultimately to provide a link for most of our data activities (see Technical Report 1). Various data activities of the Division are discussed in Technical Reports 2, 5, 12, 15-18, 21-23, and 26. The strong integration of data activities with the experimental and computational programs means that experimental efforts often arise out of needs that these data activities identify. A recent example of this is the experimental and computational efforts that arose out of the project to create a focused database for chlorination chemistry (See Technical Report 11).

Computational Chemistry

The continued increase in computing power along with robust quantum mechanical codes is making the *ab initio* calculation of chemical properties an important tool for the industrial chemist. Progress in this area, however, is hampered by the lack of standards, comparisons, and simplified methodologies. In addition to this external need, the experimental projects within the Division benefit greatly by having a strong computational component. These considerations lead us to establish a computational chemistry focus area in the Division. Thus, we have initiated projects to compile, evaluate, and disseminate information about computational techniques (See Technical Report 2) and to develop improved methodologies for calculating thermodynamic and kinetics parameters (See Technical Reports 3, 4, and 20).

Future plans include an extension into condensed phase chemistry, which will utilize the Division's capabilities in molecular dynamics (see Technical Report 29) and will be coupled with experimental efforts in solution-phase and supercritical-water kinetics (See Technical Report 6).

Data for Process and Product Design

At some point in the manufacture of almost all the products that we use, there is a chemical transformation or separation process involved. In modern industry, the products and processes are designed and optimized by process simulators. These rely on fundamental physical and chemical property data. The Division's goal is to provide the data that industry needs to effectively apply process modeling and simulation at all appropriate points in the manufacturing cycle, from the separation and treatment of raw feedstock, through the manufacturing process, to the ultimate treatment and disposal of waste streams. This has led to a wide array of projects in the Division, some of which are strongly focused on a specific problem. Areas of current interest include:

- Properties of new solvents (See Technical Report 5)
- Solvation and reactions in supercritical media (See Technical Report 6)
- Membrane and other separation techniques (See Technical Reports 7-9)
- Semiconductor processing (See Technical Report 10)
- Chlorination chemistry (See Technical Report 11)
- Carbon dioxide conversion (See Technical Report 14)

In addition to providing the basic physical and chemical property data needed for process simulation, the Division is also active in the development and application of simulation techniques applied to both reacting chemical systems (See Technical Reports 12 and 13) and complex fluid systems (See Technical Reports 27 and 28).

Properties of Energy-Related Fluids

Energy-related fluids include both those which are primary sources of energy, the fuels, and those which interconvert heat and useful work – the working fluids. In several key areas, industry requires accurate and comprehensive equilibrium and transport property data and models for these fluids. These areas include the design and optimization of working cycles in refrigeration and power production systems; the design and control of gas processes; custody transfer; and in the development of new, cleaner energy systems. Efforts in the Division to meet these needs include the development of experimental apparatus for thermophysical property measurements; the acquisition of data; and the development and dissemination of accurate correlations. Other work has focused on the thermophysical and transport properties of mixtures of alternative refrigerants with lubricants. An important facet of this focus area has been participation in the development of internationally accepted standards. Examples of activities under study in this focus area include:

- Standards for refrigerant properties (See Technical Report 15)
- Natural gas systems (See Technical Report 16)

- Hydrogen-enriched fuel systems (See Technical Report 17)
- Refrigerant transport properties (See Technical Report 18)
- Petroleum fractions and refrigerant/lubricant systems (See Technical Report 26)

Environmental Fates of Industrial Chemicals

The use of chemicals in American industry is ubiquitous, and much of the Division's efforts go toward improving these processes. The fate and disposal of these industrial chemicals and the associated byproducts are also of great concern. A wide variety of physical and chemical data is essential to understand the fate and impact of industrial chemicals in the environment, to develop strategies for the removal or destruction of harmful byproducts, or to design processes and products which minimize environmental impact. One of the considerations for choosing new data sets for inclusion into the NIST WebBook is environmental importance. Thus, in the past year Henry's law constants were added along with many new vapor pressure values (see Technical Report 1). We have carried out studies on the atmospheric chemistry of industrial compounds for many years, spanning studies of reactive species which may contribute to photochemical smog, to much less reactive species which may contribute to ozone depletion or global warming. Providing fundamental data in support of chemical disposal technologies is a relatively new activity, although it was a driving factor behind the development of a supercritical water reactor (See Technical Report 6). Technical Report 19 discusses recent results from a collaborative effort in the application of our expertise in radiation chemistry to a serious waste disposal problem. Other work in the Division includes studies of the phase equilibria, coexisting densities, and interfacial tensions of mixed electrolyte/solvent waste streams.

During FY99, we initiated a new project to leverage our experimental capabilities in atmospheric chemistry by use of new capabilities in computational chemistry. This was prompted by studies that demonstrated the shortcomings of simple structure-activity relationships. The long-term objective of this project is to establish a theoretically justified means of predicting the atmospheric reactivity of new classes of compounds with the use of a limited number of selected experimental studies for verification. Progress in this area is summarized in Technical Report 20.

Tools for Chemical Analysis

Central to all of chemistry is the analysis of complex mixtures and the identification of the individual chemical constituents. These analyses are usually derived from basic physical/chemical properties of the species, and knowledge of these properties is thus critical to the reliability of the information. The Division strives to produce evaluated data, predictive algorithms, and analysis software to assist in the identification and quantification of a range of species under diverse conditions. The NIST WebBook plays a central role in this, but current Division activities also include measurements and data acquisition designed to expand the gas chromatographic and mass spectrometric databases (see Technical Reports 21 and 22). A critically important activity in the Division is the development of complex algorithms for the rapid and automatic analysis and deconvolution of GC/MS data for the identification of chemical-weapon agents (See Technical Report 23).

Fundamental Studies of Fluids

In support of the Division mission to provide U.S. industry with thermophysical properties of gases, liquids, and solids, the Division maintains a focus area on the fundamental studies of fluids, with strong experimental and theoretical components. The goals are to develop and utilize unique experimental, theoretical, and simulation capabilities to study fluid systems under equilibrium and nonequilibrium conditions. Much of the work relates to phase boundaries, vapor-liquid and solid-fluid equilibria, including complex interactions leading to gel formation. Some of the areas the Division is focusing on are:

- Surface tension of mixtures (See Technical Report 24)
- Solid-liquid equilibrium (See Technical Report 25)
- Thermophysical properties of partially characterized systems (See Technical Report 26)
- Relationship between fluid properties and shear (See Technical Report 27)
- Radiation scattering and simulation studies of complex fluid systems (See Technical Reports 9 and 28)
- Microheterogeneity in liquids (See Technical Report 29)

In selected cases, the measurements and the calculations of the thermophysical properties of gases have been refined to make fundamental contributions to metrology. We have used very accurate measurements of the speed of sound in argon between 200 K and 300 K to determine the differences between the internationally accepted temperature scale (ITS-90) and the Kelvin thermodynamic temperature. This work is being extended to 800 K in collaboration with the Temperature Group of Division 836 (see Technical Report 30). Our *ab initio* calculations of the thermal conductivity, viscosity, and second virial coefficient of helium are now more accurate than the measurements of these properties. Thus, calculated "data" can be used to calibrate instruments made to measure these properties. With a newly funded competence program, we are improving the measurement and the *ab initio* calculation of the dielectric constant of helium. Our goal is to use gas-filled capacitors to calibrate piston gauges in the range 0.5 MPa to 5 MPa.

Cryogenic Technologies

Cryogenic technologies are critical to a wide variety of technically and industrially important areas. These include the cooling of electronics for optical sensing and high-speed computing; the production of ultra-clean vacuum environments for semiconductor and other manufacturing processes; the liquefaction of natural gas and other industrial gases on demand; and in numerous medical applications. The research of the Division in this area involves the application of thermophysical concepts and measurements for temperatures below 120 K. This research has focused primarily on improved measurement and modeling techniques involved in the development and characterization of novel and improved cryocoolers (See Technical Report 31), studies of microscale heat transfer, and the maintenance and improvement of the national standard for cryogenic flow measurements (See Technical Report 32). As part of an upgrade, the cryogenic flow loop has been brought into compliance with ISO Guide 25 requirements.

Organizational Structure

Division-Office Projects (Gaithersburg and Boulder)

- Study the behavior of fluid systems under both equilibrium and nonequilibrium conditions using unique experimental, theoretical, and simulation capabilities.

Properties for Process Separations Project (Boulder)

- Performs research and provides critically-evaluated data and models on a variety of fluid-based separation processes, including distillation, adsorption, and supercritical fluid extraction.

Membrane Science and Technology Project (Boulder)

- Performs research on characterization techniques and provides fundamental data and models needed to design and/or select more efficient and robust materials for membrane-based separations.

Fluid Science Group (Gaithersburg)

- Develops and applies state-of-the-art techniques based on acoustics and other novel approaches for measuring the thermodynamic and transport properties of fluids and fluid mixtures, including refrigerants and semiconductor processing gases.
- Performs research on next-generation primary standards in the areas of temperature, pressure, and low flow rate.

Experimental Kinetics and Thermodynamics Group (Gaithersburg)

- Develops and uses state-of-the-art measurement techniques to determine the rates and mechanisms of chemical reactions in the gas and liquid phases and the thermodynamic properties of industrially and environmentally important chemical species and materials.
- Develops new measurement methods for detecting and characterizing reactive intermediates.
- Certifies Standard Reference Materials for thermodynamic properties important to industry and science.

Chemical Reference Data and Modeling Group (Gaithersburg)

- Develops and evaluates new theories, models, and estimation methods for thermodynamic properties, rate constants, and molecular spectra
- Compiles, evaluates, correlates, and disseminates Standard Reference Data.
- Develops and disseminates electronic databases and software on thermodynamics, chemical kinetics, and analytical mass and infrared spectra.

Computational Chemistry Group (Gaithersburg)

- Develops and applies computational methods for calculating the chemical and physical properties of selected species and systems.
- Critically compares computational predictions with the best available experimental data to establish the accuracy and reliability of computational methods.
- Develops resources to provide guidance to non-experts on methods, reliability, and resource requirements.

Experimental Properties of Fluids Group (Boulder)

- Performs experimental research and develops and maintains high-accuracy apparatus for measuring the full complement of thermodynamic and transport properties of fluids and fluids mixtures over wide ranges of temperature, pressure, and composition
- Provides comprehensive thermophysical property measurements for technically important pure fluids and mixtures, including common organics and inorganics, hydro-carbons, refrigerants, and aqueous systems.

Theory and Modeling of Fluids Group (Boulder)

- Performs theoretical and simulation research on the thermophysical properties of fluids and fluid mixtures, including regions of fluid-fluid and fluid-solid phase separation.
- Develops models and correlations of high accuracy to describe and predict the thermophysical properties of fluids and fluid mixtures.
- Provides comprehensive and evaluated Standard Reference Data and electronic databases for the properties of technically important fluids and fluid mixtures.

Cryogenic Technologies Group (Boulder)

- Develops improved measurement and modeling techniques for characterizing basic cryocooler components and processes.
- Develops prototype state-of-the-art cryocoolers for specific applications.
- Provides measurement standards and services for flow under cryogenic conditions.

Staff Recognition

- **Ray Radebaugh** was awarded the J&E Hall Gold Medal from the Institute of Refrigeration for research on the development and theory of pulse tube refrigerators.
- **Eric W. Lemmon, Mark O. McLinden, and Adele P. Peskin** (895) received an SRD Measurement Service Award for their contributions to the development of the RefProp Database.
- **Steven E. Stein** was selected to receive the Patterson-Crane Award by the Columbus and Dayton Sections of the American Chemical Society for contributions to chemical documentation.
- **Michael J. Kurylo** received a Certificate of Appreciation from the United Nations Environmental Programme for his contributions to the 1998 assessment activities conducted under the auspices of the Montreal Protocol.
- **Eric D. Marquardt and Ray Radebaugh** received the Russell B. Scott Memorial Award for the Outstanding Paper in Cryogenic Engineering Research, which was presented at the Cryogenic Engineering Conference.
- **Steven E. Stein** received the 1999 ANACHEM award from the Association of Analytical Chemists, for his outstanding research achievements and service to the field of analytical chemistry.
- **Michael R. Moldover** was recognized for presenting the best oral presentation at the Seventh International Symposium on Temperature and Thermal Measurements in Science and Industry.
- **Mark O. McLinden** was selected for the NIST Slichter Award for working closely with the air-conditioning/refrigeration industries to replace ozone-depleting CFCs with environ-mentally acceptable alternatives.
- **Joe W. Magee** was given the Diversity Award for the NIST-Boulder Laboratories.
- **Michael R. Moldover and Robert F. Berg** (836) were part of a team which received the NASA Lewis Distinguished Publication Award for their paper, "Equilibration Near the Liquid-Vapor Critical Point in Microgravity," Phys. Rev. E 57, 436 (1999).
- **Patrick A. G. O'Hare** (retired) was made a Fellow of IUPAC.
- **Jan V. Sengers** has been elected a Fellow of the American Institute of Chemical Engineers for his significant contributions to the chemical engineering community.

B. Selected Technical Reports

1. *The NIST WebBook: NIST Chemical Reference Data for Industry*

W.G. Mallard, *P.J. Linstrom, J.F. Liebman (Univ. of Maryland, Baltimore County), and P.J. Christian*

Objective: To provide Internet access to a complete set of chemical data with a common interface that is both easy to use and easily expanded.

Problem: There is an enormous amount of organic thermochemical data (heats of formation, entropies, heat capacities, heats of reaction) that are largely unknown to the technical community. One part of this project is to find and evaluate those data. In addition, there is a need to make available ancillary thermochemical data such as phase-change enthalpies. Data on infrared, ultraviolet, and mass spectra are often difficult to find. For all of these data, it is essential that tools be developed to provide easy access.

Approach: It is clear that the World Wide Web has dramatically changed the way that scientific information is communicated. The use of the Web as a publishing medium and as a resource for communication has been growing rapidly. What has not followed is the development of reliable data resources for the Web. The WebBook is an effort to correct this. The WebBook provides a fast and direct source of data available at all times. The initial efforts have been tied to an approach based on compounds rather than properties. All the data on benzene, for example, are gathered together, rather than all the data on heat of combustion. While the major thrust of the WebBook is to supply data from NIST evaluations, the role of the WebBook in providing a resource for chemical data from all sources will expand. In parallel with the efforts to gather and evaluate data, another major part of this project is aimed at providing the mechanisms needed to make these and other NIST chemical reference data available on the Internet. These efforts are part of NIST's program on Systems Integration for Manufacturing Applications (SIMA).

Results and Future Plans: During FY99 the fifth edition of the NIST Chemistry WebBook* was released. The total number of compounds for which data are provided has steadily increased and in the fifth edition, data for more than 31,800 compounds are available. As with every previous release, new data types were added; specifically, Henry's law data and UV/Visible spectral data. In addition, new data on critical constants, vapor pressure, and ion energetics were added, as well as significant increases in many of the thermodynamic data types. A new tool for substructure searching using chemical structures drawn by the user has been added. The number and variety of users—in industry, government, and academia—are a clear indication of the need for this type of service. Between 6000 and 12000 users per week use the Chemistry WebBook, an increase of about 25% from last year; and the fraction of returning users is between 45% to 55%. The WebBook is also a tool to aid future evaluation projects both at NIST and in collaboration with others. The goal of this project is to have a single point of entry for access to all chemical data at NIST. It is anticipated that during FY 2000, there will be two releases of the NIST WebBook. Additional data as well as new searching software will be included.
*http://WebBook.nist.gov

Publications:
Linstrom, P.J. and Mallard, W.G., ***"The NIST WebBook: A Tool for Chemical Data Access on the Internet,"*** Proceedings of the 10th International Chemical Information Conference and Exhibition, Nimes, France, October 18-21, 1998.

Mallard, W.G., and Linstrom, P.J., eds., ***"The NIST Chemistry WebBook,"*** http:\\WebBook.nist.gov.

2. *Computational Chemistry Comparison and Benchmark Database*

R.D. Johnson III

Objective: (1) To provide a benchmark set of molecules and reactions for the evaluation of *ab initio* computational methods. (2) To allow the comparison between different *ab initio* computational methods and experiment for the prediction of thermochemical properties. This will allow accuracy in the computed thermochemical properties to be estimated.

Problem: As computer power increases, there is more reliance on modeling and computational chemistry in the chemical industry. This use is owed to the increased safety and speed, and decreased cost of models and calculations when compared with laboratory measurements. This trend will continue as the computers and software become more powerful. *Ab initio* computational chemistry methods can provide accurate values for structures, entropies, and heats of formation. However, the cost of the calculation increases greatly as the accuracy increases. The errors in the computational methods are systematic, depending on the method and functional groups that compose the molecule. In order to take advantage of the computational methods, accuracy and cost need to be evaluated. A set of test molecules is needed for this evaluation. There are small sets of species for comparing theory and experiment [L. A. Curtiss *et al.*, J. Chem. Phys. 109, 42 (1998)], but a recent workshop on Computational Thermochemistry at the ACS 212th National Meeting identified the need for a larger set of species, on the order of 500.

Approach: In order to facilitate testing, we selected a set of benchmark molecules and reactions with reliable thermochemical and spectral data and for which both the values and the uncertainties had been evaluated. These measured data include gas-phase enthalpies of formation, entropies, vibrational frequencies, and structures. In addition, we are generating data from *ab initio* calculations for comparison with experiment. The calculations cover eighteen methods using six basis sets.

The presentation will be through a Web interface where a user can select a subset of molecules from the database (*e.g.*, all species containing phosphorus or an NH_2 group), and the property for comparison (*e.g.*, heat of formation). The user will be presented the experimental and calculated values as a table or chart. By comparing the experimental and computed thermochemical values for a given set of molecules, the systematic errors in the computed values can be determined.

Results and Plans: A set of over 600 species with well-known enthalpies of formation has been assembled. Both experimental and calculated values are accessible over the web. Tools are being developed for viewing and accessing this data, such as comparing experimental or theoretical enthalpies of atomization at a given temperature, and comparing reaction energies for user-specified reactions. Experimental data are being collected and evaluated. *Ab initio* calculations are ongoing. In addition to heats of formation, structures and vibrational energy levels are being included. Beta testers are reviewing the database now. (Web site: http://srdata.nist.gov/cccbdb/).

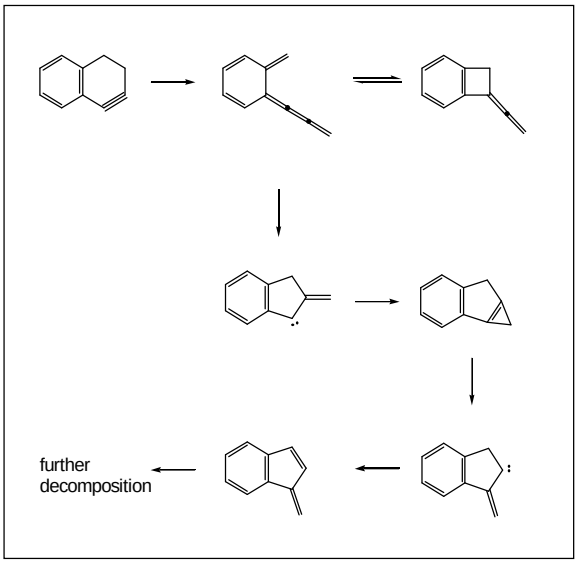
3. *Automated Predictions of Chemical Reactions and Their Mechanisms*

***K.K. Irikura** and R.D. Johnson III*

Objective: To predict the reactivity of molecules.

Problem: Chemical reactions are of essential and fundamental importance throughout chemistry and related technologies. Although experienced chemists can sometimes predict the reactions that will occur in a new chemical system, they may overlook some alternatives. Moreover, they are usually unable to make reliable predictions when the chemistry in question is unfamiliar to them. As more exotic chemicals and materials are investigated, this situation is increasingly common. Yet there are few tools available to assist in predicting chemical reactions, and none at all for predicting the novel reactions that are of greatest interest.

Approach: Quantum chemical calculations can predict how the energy of a chemical system changes as its constituent atoms move. This energy function, known as the potential energy surface (PES), contains all the information about the chemical reactions that are thermally possible in that system. Searching the PES will provide predictions of all those reactions. However, a typical PES has a high dimensionality, making it too large to search exhaustively. Thus, in practice it is impossi-



The starting compound was prepared in the hope that it would undergo the phenylcarbene rearrangement. However, isotopic labeling experiments, combined with the experience of the experimenters, indicated the mechanism shown above. It was recovered computationally using isopotential searching.

ble to find all possible chemical reactions. Nonetheless, by restricting the search to a contour of constant energy (isopotential), it is possible to find at least some reactions. Thus, this technique is a useful tool to supplement the predictions of a human expert.

Results and Future Plans: Several algorithms have been designed to implement the general task of isopotential searching, including one that is well suited for large-scale parallelization. Prototype software has been written and used to test the technique. The first tests were for chemical reactions that were predicted incorrectly by experts, with the correct results discovered later. In all cases, the correct reaction mechanisms were successfully produced by isopotential searching methods. A complex example is shown in the figure. In the future, we will (1) test the procedures on other reactions that are already known but that represent different types of chemistry (*e.g.*, transition metals), (2) apply the methods to make new predictions for important systems, and (3) distribute the software as appropriate.

Publication:

Irikura, K.K. and Johnson, R.D., III, ***"Predicting Unexpected Chemical Reactions by Isopotential Searching,"*** J. Phys. Chem. A (in press).

4. *Development of a General Purpose Geometry Optimizer for Large-Scale Molecular Systems*

C. Gonzalez *and T. Allison*

Objective: To develop and implement efficient geometry optimization algorithms aimed at the characterization of potential energy surfaces of large-scale molecular systems.

Problem: Recent advances in the efficiency of computational methodologies used in the evaluation of molecular energies and derivatives have created a need for efficient geometry optimization techniques. This need is particularly evident as the computational chemistry community attacks problems of increasing size and complexity such as biomolecules and reactions in condensed phases. While some of these techniques have appeared recently in the literature, they are typically integrated into specific codes and are not portable to other packages, restricting their access to a limited population of the scientific community. In addition, careful evaluation of the current geometry optimization packages has pointed to a marked lack of "user-friendly" tools that can aid in the semi-automated search for stationary points on potential energy surfaces of large molecules. Most of the time scientists need skills comparable to those of an expert in geometry optimization to tackle these problems. Given the increasing popularity of computational chemistry software in the study of a large variety of chemical problems, it is therefore necessary to build the appropriate infrastructure that will allow scientists to characterize the corresponding potential energy surfaces with a minimum of effort.

Approach: To address these needs, a general-purpose program with efficient optimization algorithms tailored for large molecules has been created. The program, called TURBO-OPT, performs geometry optimizations using energy derivative information from a variety of computational chemistry codes through a simple interface that gathers the necessary information from the normal outputs generated by these programs. This feature allows scientists to perform geometry optimizations using a common software platform that interfaces to the different theoretical methodologies available in common quantum chemical and molecular mechanics programs. For the advanced user, TURBO-OPT offers the necessary machinery to test and

validate the different geometry optimization algorithms available in the literature.

Results and Future Plans: The current implementation of TURBO-OPT locates global and local minima, transition states, and reaction mechanisms. So far, the interface allows the use of two popular quantum chemistry codes. Preliminary tests, conducted on a series of 32 molecules with different degrees of freedom (5 – 500), show that the geometry optimization algorithms contained in TURBO-OPT provide substantial computational savings relative to conventional algorithms available in the literature. Efficiency in the algorithms is being improved and new features are being implemented. In addition, the interface will be extended so the program can be used with other computational chemistry packages. An alpha version of TURBO-OPT will be distributed among the members of the Computational Chemistry Group as well as selected scientists within NIST for validation purposes. It is expected that enough feedback will be gathered from the testing phase so that the current features of the program can be improved and extended to satisfy the demands of novice and advanced users.

5. *Measurements, Modeling, and Database Development for the Application of Alternative Solvents*

T.J. Bruno *and A.F. Lagalante*

Objective: To develop and test predictive models for solvation of compounds in alternative solvents at supercritical, near-critical, and subcritical conditions using a combination of both physical and chemical variables as input into an empirical multivariate statistical model.

Problem: The most important thermophysical parameter required to assess the feasibility of an extraction process is the solute-solvent phase equilibrium. Serious limitations exist in equation-of-state approaches that use only physical properties of the solute and solvent to model phase equilibrium.

Approach: Safe replacements for conventional solvents are likely to come from fully or partially fluorinated alkanes, ethers, or ketones that possess negligible ozone depletion potential, as well as functionalized glycol ethers and siloxanes. Many of the fluorinated alternative solvents are gases under ambient conditions, and their thermophysical properties offer the promise of both conventional liquid extraction and the tunable solvent strength offered by near-critical and supercritical fluid extraction. In our approach, a given solution process is empirically modeled as the dependent variable in a multivariate statistical analysis. The independent variables to the multivariate statistical model include empirical solute-solvent interactions and additional state-dependent terms. Solute-solvent interactions are quantified using empirical solvatochromic and chromatographic parameters of acidity, basicity, polarizability, and polarity. These parameters represent the dominant chemical interactions in solvent-solute systems and will account for contributions to the nonideal portion of phase equilibrium. Accounting for these interactions will permit higher accuracy than EOS approaches. The statistical model aids in the identification of alternative solvents by making it possible to predict the solubility of industrially relevant compounds.

Results and Future Plans: In recent years, we have designed and constructed numerous spectroscopic, chromatographic, and gravimetric instruments for the measurement of solubilities of solutes in sub- and supercritical fluids. Solutes studied have ranged from classes of organometallic compounds to physiologically active natural products. The solvatochromic parameters for the fluorinated ethane solvents have been measured using high-pressure spectroscopic cells. Values are density-dependent over the gas-to-liquid density range and have been used to model R143a/water, R134a/water, and carbon dioxide/water partitioning of organic solutes. Parameters for the glycol ethers, alkanolamines, and siloxanes have been measured for both the pure compounds and aqueous solutions. Soon, we will be developing a fiber-optic solvatochromic sensor to facilitate measurement of solvatochromic parameters. The sensor will allow the rapid measurement of solvent mixtures for determination of mixture parameters. Pure component and mixture parameters will be incorporated into a database that will allow researchers to statistically model an industrially pertinent solvent replacement technology. The database model will suggest suitable alternative solvents and extraction conditions to substitute for a hazardous solvent.

Publications:

Lagalante, A.F. and Bruno, T.J., ***"Modeling the Water-R143a Partition Coefficients of Organic Solutes Using a Linear Solvation Energy Relationship,"*** J. Phys. Chem. 103, 7319 (1999).

Lagalante, A.F., Hall, R.L. and Bruno, T.J**., *"Kamlet-Taft Solvatochromic Parameters for the Fluorinated Ethane Solvents,"*** J. Phys. Chem. B 102, 660 (1998).

Lagalante, A.F., Wood, C., Clarke, A.M. and Bruno, T.J., ***"The Kamlet-Taft Solvatochromatic Parameters for 25 Glycol Ether Solvents and Glycol Ether Aqueous Solutions,"*** J. Sol. Chem. 27, 887 (1998).

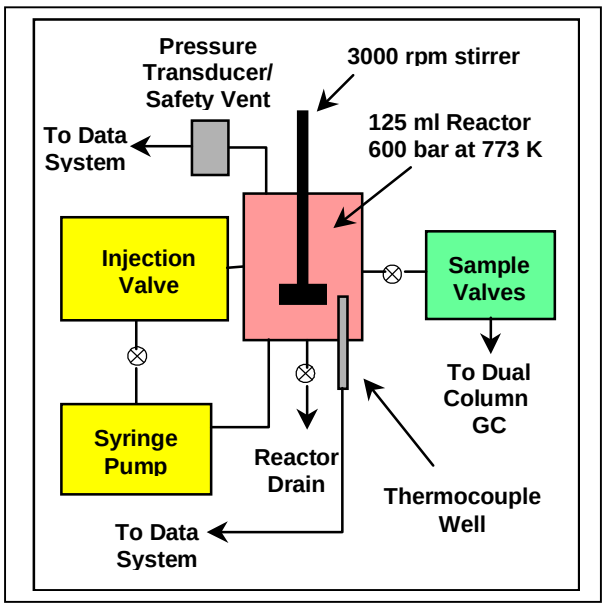
6. *Chemical Kinetics in Supercritical Water*

J.A. Manion, *V. Anikeev, R.E. Huie, and W. Tsang*

Objective: To develop an experimental apparatus to obtain transferrable information on the rates and mechanisms of a variety of chemical reactions in supercritical water (SCW).

Problem: The physical properties of water change rapidly near its critical point (374 °C, 221 bar). One result is that rates and mechanisms of chemical reactions can be strongly affected by small changes in process variables. This makes the supercritical environment extremely interesting for use in hazardous waste destruction, the oxidation of biomass and metabolic wastes, and the development of new chemical synthesis strategies. A detailed understanding of the chemical reactions of organic compounds in SCW remains lacking, however, in part due to significant experimental difficult. For instance, the limited solubility of most organics in sub-critical water causes mixing difficulties and can necessitate complex corrections for diffusion. A more serious problem is that many reactions are faster in hot, dense water than in the supercritical environment. Classic static and flow systems involve long heat-up and cool-down times during which the organic is in contact with hot water. This can lead to spurious or ambiguous results. Finally, a widely applicable analytical system is needed, suited to studies of reactions about which little is known. Traditional post-reaction analysis, however, is both time-consuming and difficult in SCW studies because of phase separation of gases and of polar and non-polar liquids.

Approach. We have designed and built an innovative reactor that overcomes many experimental deficiencies of previous approaches. A schematic of the reactor is shown at right. The 125 mL static reactor is rated to 773 K and 600 bar, sufficient for studies with water densities ranging from gas-like to those approaching liquid water. The reactor features precise temperature and pressure controls and a stirrer rated to 3000 rpm. Water is added into the reactor using a high-pressure syringe pump. To avoid studying "hot water" chemistry, the organic of interest is injected directly into the pre-existing SCW environment. An automated high-pressure valve and loop system allows withdrawal and storage of micro-scale samples (6 μL) without perturbing the reactor conditions. Separate analyses of light gases and heavier components are performed on the dual-column GC. Sequential analyses allow the time progression of the reaction to be easily followed in a single experiment, vastly improving the efficiency of data collection.



Results and Future Plans. Systematic studies of the reversible dehydration of alcohols are underway. Results to date show that the rate of reaction is much faster in SCW than in the gas phase and is highly dependent on the density of the fluid. These observations suggest that ionic processes are important and occur even at relatively low fluid densities (0.2 g/cm^3). It is interesting to note that the reaction in SCW is significantly *slower* than in hot water. This demonstrates the importance of direct sample injection to obtain the correct kinetic parameters. Studies are being extended to other reaction classes involving hydrolysis and molecular

reactions. In conjunction with the experimental program, we are collaborating with NIST molecular modelers and computational chemists to develop better theoretical models of reactions in SCW.

7. *Liquid, Vapor, and Gas Transport Properties in Membranes and Films*

***J. Pellegrino**, X. Yi, J. Portnoy, K. Nerbonne, and T. Rasco; O. Stange (GKSS Research Center); and M. Guiver (National Research Council of Canada)*

Objective: To develop improved measurement methods for obtaining diffusion and solubility of liquids, vapors, and gases in membranes and films, to elucidate transport mechanisms and quantitative structure/transport property prediction methods for membrane materials (especially polymeric) based on high quality measurements of sorption and transport in several well-characterized systems, and to compile property data on industrially important materials used for membrane-based separations.

Problem: Although polymeric and inorganic materials are used in membrane and adsorptive separation processes, a significant barrier to the optimum use of existing materials and development of new materials is the lack of predictive capabilities for the transport properties of mixtures in any selected material. Improved processes for obtaining high-purity oxygen and nitrogen from air, processing natural gas, recovering hydrogen from refinery streams, recovering and purifying olefin streams, and purifying water are examples of important industrial uses of membranes.

Approach: This program has measurement, modeling, and database components. Measurements of liquid, vapor, and gas diffusion and sorption in thin layer films are critical for development of techniques to predict membrane transport properties. These measurements provide a means to include the effects of both chemical and structural subgroups in the material, and ultimately, to delineate rational design criteria for separations. Through our collaborations we have access to materials for which chemistries are well studied and/or can be varied in well- defined ways. In addition, the polymers currently under study (polypropylene, cellulose acetate, polysulfones, polyperfluorosulfonic acid, polytrimethylsilyl-propyne, and polyaniline) represent both commercial and newly developed materials. This research program also includes the development of an internet-accessible database of polymeric material properties important for membrane separation design.

Results and Future Plans: A flow cell equipped with attenuated total reflectance (ATR)-FTIR and an accurate flow control and measurement system has been developed to measure diffusion of multicomponent mixtures in films. Two techniques for making measurements on pre-made films (necessary for making measurements on commercial membranes) have been developed. Using one of the techniques, measurements of water and acetone mixtures diffusing from the liquid state into a commercial polypropylene (PP) film have shown that (1) water must lose its H-bonding before entering PP and (2) in a mixture, acetone diffusion is coupled with water and speeds up the process. The second technique, using a thin (<0.5 μm) adhesive layer (*e.g.*, of a mineral or fluorochemical oil) to maintain good optical contact between a pre-made film and the ATR crystal, will facilitate measurements with gas mixtures. The sorption program includes four sorption apparatus (based on pressure decay methods) that, during the past year, were used to determine the film density of polyvinyl alcohol-modified with cyclodextrin side groups. A surface acoustic wave device will be brought into service during the coming year with the ultimate objective of combining it with the ATR-FTIR flow cell for multicomponent gas and vapor transport measurements. An initial version of the membrane technology database, containing unevaluated gas transport properties on hundreds of polymers, has been completed and is accessible via the internet.* This work begins to address a need within the chemical engineering community for comprehensive, critically evaluated information on separation membranes, and how these membranes interact with important chemical feedstock components. The database includes permeability, solubility, and diffusion coefficients; ideal and mixed gas separation factors; temperatures; primary reference; monomer repeat unit structure; and common names and abbreviations. Future work will expand the number of polymers and include predictive models.

*(http://www.membranes.nist.gov).

8. *Measurements and Data for Pressure-Driven Membrane Separations*

***J. Pellegrino**, E.J. Han, and M. Lewis; G. Amy, J. Cho, Y. Yoon, P. Brandhuber, S. Wright, and S. Delagah (Univ. of Colorado); and M. Chapman Wilbert and K. Price (U.S. Bureau of Reclamation)*

Objective: To develop improved quantitative characterization techniques and predictive models for the filtration of complex mixtures using commercial membranes based on high quality measurements of streaming potential and water transport coefficients and detailed measurements of filtration results on dilute, complex aqueous mixtures encountered in membrane-based separations.

Problem: The first commercially viable, synthetic membranes suitable for molecular scale separations (reverse osmosis, nanofiltration, and ultrafiltration) were developed over twenty-five years ago. However, research during the intervening years has not developed a systematic approach for matching membranes to complex mixtures and predicting the filtration figures-of-merit: species partitioning into the membrane (rejection), solvent (water) permeability, and permeability decline with time. Improved processes for obtaining specialty chemicals, pharmaceuticals, and advanced monomers using environmentally benign processes, and more economic ways to recover, reuse, and supply water are examples of important industrial and municipal uses of membranes.

Approach: This program has both measurement and modeling components. Meaningful and accurate measurements on both the membrane and the complex mixtures are required in order to develop a systematic correlative approach. These measurements provide a means to combine the effects of chemical, physical, and structural characteristics of the membrane and the mixture, and ultimately, to delineate rational design criteria for separations. Through our collaborations with the U.S. Bureau of Reclamation and the University of Colorado, we are developing new test protocols, refining existing characterization techniques, and developing a database of consistent measurements of filtration figures-of-merit and membrane and mixture characteristics. This database is being compiled to facilitate the development of correlative models for matching membranes to specific applications.

Results and Future Plans: This year we have used our improved protocol for measuring the tangential flow streaming potential of membrane sheets. This technique is commonly used to characterize the relative surface energy and charge at the membrane interface. We are measuring streaming potential as a function of electrolyte composition, concentration, pH, and temperature. These data will be used in a model to calculate the surface potential of the membrane or film. The membrane's surface potential will then be incorporated into materials research, manufacturing quality control, and engineering design models. We have continued development and testing of a new apparatus to measure the kinetics of solvent diffusion through membranes. This apparatus has a resolution on the order of 10^{-8} L/s and may provide an improved method for absolute characterization and monitoring of very subtle structural changes in membrane materials, caused by aging, exposure to chemicals, and mechanical trauma. We were able to successfully use this apparatus to identify small structural changes in reverse osmosis membranes exposed to dilute NaCl solutions versus control samples. We have extended our filtration database measurements beyond natural organic matter filtration to include trace hazardous species, for example, arsenate, arsenite, and perchlorate ions, and colloidal particles. We have also developed a semi-empirical model for modeling and predicting flux decline in macromolecule filtration that is mostly based on parameters that may be measured independently or estimated from physicochemical properties of the solutes.

Publication:

Chapman-Wilbert, M., Delagah, S., and Pellegrino, J., ***"Evaluation of Variance in Streaming Potential Measurements,"*** J. Membrane Sci. 161, 247 (1999).

9. *Structure, Adsorptive Separations, and Characterization of Surfactant/Clay Complexes*

***C.D. Muzny**, T.J. Bruno, and H.J.M. Hanley*

Objective: To exploit the unique characteristics of clay platelets in the production of organic-inorganic composite materials with revolutionary material properties and in the development of novel chemical separation techniques.

Problem: Clay is the key inorganic substance in applications ranging from pollution prevention and remediation, enhanced oil recovery, the treatment of petroleum liquids, the manufacture of cosmetics and pharmaceuticals, and the synthesis of polymer nanocomposite materials. An understanding of clay-organic chemical interactions and the effects these interactions have on the structure of clay complexes is a key issue for future developments in all of these applications.

Approach: Our approach is twofold. First, in order to understand the structural changes induced by clay surface treatments, we are undertaking a small-angle neutron scattering and dynamic light scattering investigation of the complexes formed in mixture suspensions of clay mineral and cationic surfactants. These techniques allow us to monitor the changes in the nanoscale structural properties of clay and organoclay complexes in a variety of situations. Second, in order to understand the chemical kinetics of the clay-organic interaction, we have advanced the application of physicochemical gas chromatography by devising stable clay- and organoclay-coated capillary columns. The capillary column approach that we have developed is more efficient, requires lower column temperatures, and produces values of the enthalpy of adsorption (H_{ads}) with a much lower uncertainty than the conventional techniques.

Results and Future Plans: Our results are wide ranged. For example, they include elucidation of the surface structure of synthetic clay Laponite with cetyltrimethylammonium bromide (CTAB) complexes; determination of the effect of a mineral surface on micelle formation; investigation of the effect of shear on colloidal gel formation using an adapted Couette cell of a constant stress rheometer which is placed in the neutron or light beam; investigation of the formation and structure of complexes of organic macromolecule adsorbed on an inorganic substrate; and investigation of dispersion and flocculation in aqueous mineral systems. We have also determined H_{ads} for a family of hydrocarbons on Laponite and Laponite complexed with CTAB by application of the organoclay-coated capillary column gas chromatography technique. The CTAB-coated Laponite is especially significant in the environmental context in that it represents a surrogate soil system and can be used to understand the interaction of pollutants on soils.

Future plans are to investigate further the relationship between the structure and rheology of gelling systems; to attempt to construct and characterize clay nanocomposites formed in an organic medium; and to understand better the role of an organic surface on flocculation mechanisms. We would also like to co-ordinate the structure surface studies with the thermodynamic information obtained from the coated capillary column. In addition, our future plans include extending the chromatographic technique to the measurement of the diffusion of pollutants into the clay and organoclay system.

Publications:

Bruno, T.J., Lewandowska, A., Tsvetkov, F., and Hanley, H.J.M., ***"Determination of Heats of Adsorption on a Synthetic Clay by Gas-Solid Chromatography Using a Wall Coated Open Tubular Column Approach,"*** J. Chromatogr. A 844, 191 (1999).

Hanley, H.J.M., Muzny, C.D., and Butler, B.D., ***"Surface Adsorption in a Surfactant/Clay Mineral Solution,"*** Int. J. Thermophys. 19, 1155 (1998)

10. *Thermophysical Properties of Gases Used in Semiconductor Processing*

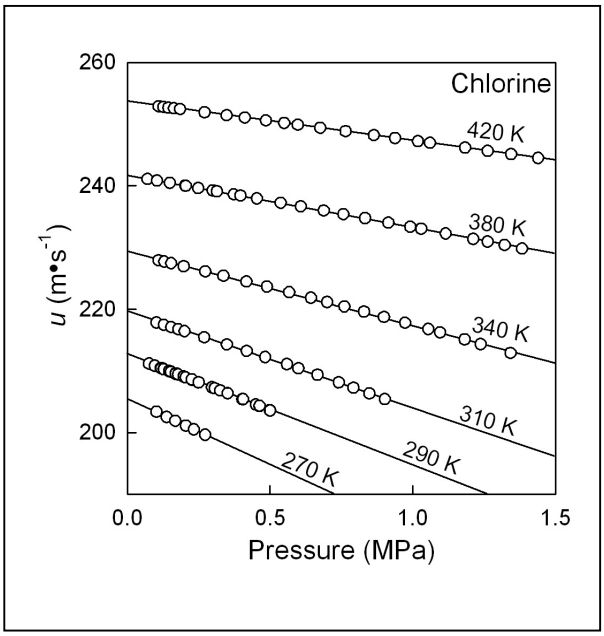
***J.J. Hurly**, K.A. Gillis, and M.R. Moldover*

Objective: To provide high-accuracy data for modeling chemical vapor deposition (CVD) and for calibration of mass flow controllers (MFCs) used in semiconductor processing.

Problem: Many process gases are toxic, corrosive, and/or pyrophoric. For such gases, measurements of thermophysical properties are sparse and rarely accurate. But accurate data are required to model the hydrodynamics of the gas streams, *i.e.*, the velocity and temperature profiles in the vicinity of the hot susceptor, and the hydrodynamics that evolve within the streams used in CVD processes. MFCs are used to deliver process gases (*e.g.*, Cl_2, HBr, BCl_3, WF_6) for CVD and for other processes (*e.g.*, plasma etching). Calibrated MFCs are needed to scale processes up from prototype to pilot plant and to production. Although MFCs are used with process gases, they are sold with calibrations for surrogate gases. Because the operation of MFCs depends upon heat transfer, converting the calibration from a surrogate gas to a process gas requires the heat capacity, thermal conductivity, density, and viscosity as functions of temperature and pressure.

Approach: We are using acoustic techniques to measure the thermophysical properties of three classes of gases: (1) binary mixtures of CVD carrier gases with process gases, (2) pure process gases, and (3) surrogate gases. We will develop a comprehensive, reliable database for these gases that provides the heat capacity, thermal conductivity, viscosity, and the pressure-density-temperature relation for the gases and also diffusion coefficients for mixtures of the gases. The diffusion coefficient will be obtained from models for the intermolecular potentials between the carrier and the process gases.

Results and Future Plans: We developed a facility for safely measuring the properties of these hard-to-handle gases. During the past year, we have completed measurements on the seven gases identified by the SEMATECH MFC Working Group as having the highest priority. The figure displays speed-of-sound data for chlorine. The data range from somewhat below the boiling temperature to 200 °C and from 25 kPa to 1500 kPa or 80% of the vapor pressure. The data were analyzed for the ideal-gas heat capacity and the equations of state with uncertainties of approximately ±0.1%. For all seven gases, effective pair potentials have been derived and these pair potentials have been used to estimate the transport properties of these gases. In the coming year, the speed-of-sound will be measured in an organometallic gas and in other process gases. Acoustic measurements of the transport properties and a database are planned.



Publications:

Hurly, J.J., ***"Thermophysical Properties of Gaseous CF_4 and C_2F_6 from Speed-of-Sound Measurements,"*** Int. J. Thermophys. 20, 455 (1999).

Hurly, J.J., Defibaugh, D.R., and Moldover, M.R., ***"The Thermodynamic Properties of Sulfur Hexafluoride,"*** Int. J. Thermophys. (in press).

Hurly, J.J., ***"Thermophysical Properties of Gaseous Tungsten Hexafluoride from Speed-of-Sound Measurements,"*** Int. J. Thermophys. (in press).

11. *Experimental and Theoretical Determinations of the Mechanisms, Kinetics, and Thermochemistry of Chlorinated Species*

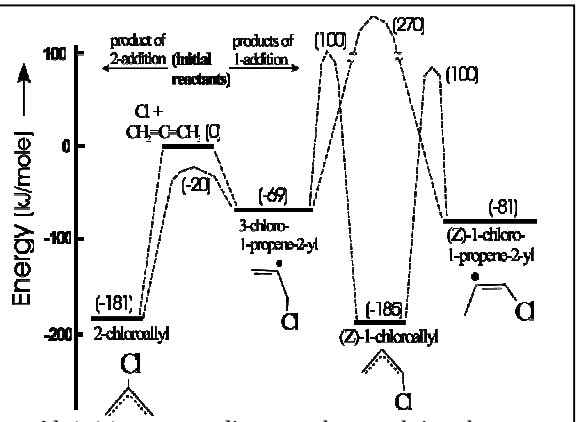
***J.W. Hudgens**, J.A. Manion, C. Gonzalez, K.K. Irikura, and T.C. Allison*

Objective: To measure and predict the reaction mechanisms, kinetics, and thermochemistry of C_3 (and larger) chlorinated species.

Problem: Within incinerators and plasmas, the reactions of chlorine with unsaturated C_3 chemical species are believed to engage in sequences that synthesize highly chlorinated by-products and pollutants. Yet, when attempting to formulate a numeric model that describes the production of such chlorinated species, one finds that no reliable reaction mechanisms, rate coefficients, or thermochemical data are available. The absence of such data persists because many practical obstacles have hindered experimental measurements of these properties. Moreover, in the absence of benchmark experimental data, the *ab initio* computational community has generally ignored the entire chemical class of C_3 chlorinated species, and thus, no broad overview for these species exists.

Approach: The research acquires new experimental kinetic and thermochemical data and involves extensive, state-of-the-art *ab initio* calculations, enabling interpretation of the data. We attempt to formulate or adapt models that allow us to predict trends across the entire chemical class. Cavity ring-down (CRD) absorption spectroscopy is used to measure real-time kinetic data and gas-chromatography/mass spectrometry (GC-MS) is used to measure the reaction end-products. The *ab initio* methods use density functional, M ller-Plesset, and multi-reference codes and formulations involving isogyric and isodesmic reactions.

Results and Future Plans: Two successful studies have shown: (1) new insights into the reactions of chlorine atoms with unsaturated C_3 species and (2) the inability of older theories to predict the properties of perchlorinated compounds. In the first study, we used CRD and GC-MS experiments to measure the reaction rate coefficients and end-products of the reactions, Cl + allene and Cl + propargyl chloride. Both reactions form energized radicals that isomerize before forming products. By using *ab initio* calculations to predict each governing reaction surface (*e.g.,* figure), we could accurately predict the observed products and confirm the governing mechanisms. The work also lead to new thermochemical enthalpies for several chlorinated C_3 radicals and stable species.



Ab initio *energy diagram that explains the products observed from Cl + allene.*

The second study tested the accuracy of the widely-used "group additivity" tools for predicting the enthalpies of formation, $\Delta_f H^\circ_{298}$, for C_1, C_2, and C_3 chlorocarbons. This research compared experimental enthalpies with those predicted by extensive *ab initio* calculations and several group additivity methods. Of particular interest was the recently determined $\Delta_f H^\circ_{298}$ for perchloropropene which provided a rigorous test for these predictive methods. In short, this extensive work found that modified group additivity works well for C_2 species, but no group additivity method gives reliable values of $\Delta_f H^\circ_{298}$ for highly chlorinated C_3 species.

12. *Evaluated Data and New Computational Tools for Chemical Reaction Engineering*

D.R. Burgess

Objective: To develop computational tools that utilize thermochemical and chemical kinetic data for the modeling of chemical mechanisms, and to validate these tools through comparison with evaluated data.

Problem: Many computational tools used in chemical reaction engineering have limited ability to assign rigorous quantitative uncertainties to the results of the calculations. In addition, the evaluated data for benchmarking the computational models are often not readily available.

Approach: Data are evaluated for developing robust chemical kinetic measurements. This evaluation involves a synthesis of experimental data and computational predictions as a means of verifying the quality of the data. The primary goals are to provide high quality thermochemical functions and rate expressions. A secondary focus is to determine procedures for providing quantitative uncertainties to values that are traceable to *ab initio* calculations (energetics) and solutions to the master equation (rate expressions). We are also developing tools for managing the thermochemical and chemical kinetic data necessary for reacting flows simulation and for reaction path analysis and mechanism generation/reduction.

Results and Future Plans: Current systems of interest are hydrocarbon combustion and halogenated hydrocarbon destruction chemistries. We have compiled, calculated, and evaluated thermochemical data for the C_1 and C_2 fluorinated hydrocarbons. We have compiled experimental rates of reactions and calculated *ab initio* transition states for HF elimination pathways from the fluoromethanes and fluoroethanes. The geometries and energies of the transition states are determined from high-level *ab initio* quantum chemistry calculations employing the G2 and CBS methods. The transition states are then used as inputs to master equation calculations, which yield temperature and pressure dependent rate expressions. We have had significant success in validating the calculated rate expressions against experimental data and have identified previously unrecognized decomposition channels. We have now begun *ab initio* transition state calculations for thermal decomposition of the C_1 and C_2 chlorinated hydrocarbons.

In a related effort, we are working with Reaction Design Corporation in (1) developing database tools for managing the thermochemical and chemical kinetic data needed in reacting flows simulations; (2) implementing Deterministic Equivalent Modeling Method (DEMM), a recently developed computational tool, which provides quantitative uncertainties for simulation results if uncertainties are input for the thermochemical and chemical kinetic data; (3) implementing computational tools for reaction path analysis and mechanism generation/reduction (*e.g.*, Principal Component Analysis); and (4) assigning computationally useful uncertainties to recommended rate expressions for hydrocarbon combustion chemistries for use in DEMM-based calculations.

13. *Fundamentals of Fire Suppression Through Computer Simulations*

***W. Tsang**, V. Babushok, and D.R. Burgess*

Objective: To develop an understanding of fire suppression from a fundamental point of view and to make contributions to efforts to find replacements for presently used agents through the use of computer simulations.

Problem: The phase-out of traditional fire suppressants owing to the effect of these suppressants on the ozone layer has led to much interest in alternative compounds. The traditional method for discovering new suppressants is through empirical testing. Computer simulations represent a potentially new tool to expand and focus experimental efforts.

Approach: With the increasing availability of powerful computational tools, the prerequisite for accurate results from computer simulations is a reliable data base of the rate constants for the fundamental chemical interactions and the thermodynamic properties of the compounds responsible for the suppression process. These were determined from an evaluation of direct experimental measurements and through the use of various estimation methods. As much as possible, results were validated through comparisons with test results carried out in the Fire Research Group at NIST. Various possible markers for suppressant effectiveness were examined. Fits with experimental results were optimized. The op-

timized model was then used to answer a number of general and long-standing questions on the nature of fire suppression.

Results: The decrease in laminar flame velocity as a function of additive concentration is used as a measure of suppressant efficiency. Simulation studies and a detailed examination of the chemistry confirmed that the changes are a consequence of the reduction of the active flame radicals such as H, OH and O and that the existence of catalytic cycles controls the effectiveness of a suppressant. Thus although fluorine can remove hydrogen atoms, the hydrogen fluoride that is formed cannot be recycled. In contrast, for a bromine compound, in the sequence of reactions $H+HBr=H_2+Br$ and $Br+RH=HBr+R^*$, HBr is acting as a catalyst. The existence of a reliable model is especially valuable in answering broad questions and for setting limits and directions of future work. The relative importance of chemical and physical effects on fire suppression can be easily settled by simply "turning off" the chemistry. For CF_3Br, the chemical component is responsible for about 80% of the initial decrease in the flame velocity. Inversely, one can "turn on" the chemistry. We found that under such conditions, one must have concentrations in the high tens or low hundreds ppm. Such a criterion is in fact met by iron compounds. A consequence of this is that the mechanism for inhibition for such compounds cannot involve gas-solid reactions. Condensation will lead to a further decrease in suppressant concentration, and rate constants are already at a maximum. Indeed, the modeling shows that the condensation of iron compounds leads to a decrease in suppressant efficiency. Another interesting issue is the applicability of experimental and modeling data carried out with a particular fuel to other fuels. Through sensitivity analysis with a variety of fuels, we demonstrate that in practically all cases the decrease in the flame velocity was controlled by the same set of reactions. This finding justifies the use of a universal ranking of suppressant activity.

14. *Photochemical Reduction of CO_2 Catalyzed by Metal Complexes*

***P. Neta** and J. Grodkowski (Guest Researcher)*

Objective: To obtain kinetic and mechanistic information on the elementary reactions involved in the photochemical reduction of CO_2 and to develop strategies for conversion of CO_2 into a fuel or feedstock materials.

Problem: Accumulation of CO_2 in the atmosphere from the burning of fossil fuels leads to global warming. It would be advantageous to reduce the amount of CO_2 by converting it into useful chemicals. Reduction of CO_2 can form various compounds including, CO, HCOOH, CH_2O, CH_3OH, and CH_4.

Approach: Iron and cobalt porphyrins and related compounds are studied as catalysts for photochemical reduction of CO_2. Our approach is to attempt to use them in photochemical systems, to demonstrate formation of CO and/or HCOOH from CO_2, and then to examine the mechanism of catalysis and to determine the relevant rate constants by pulse radiolysis.

Results and Future Plans: We have found that iron and cobalt metalloporphyrins (MP) act as effective catalysts for the photochemical reduction of CO_2 to CO and formic acid in dimethylformamide or acetonitrile solutions containing triethylamine as a reductive quencher. In these solutions, $M^{III}P$ is reduced ultimately to M^0P, which reacts with CO_2 to form CO. In these photochemical studies, the quantum yields were low. In a recent study we have shown that the yield can be dramatically increased by the use of *p*-terphenyl (TP) as a photosensitizer. TP is very effectively photoreduced by triethylamine (TEA) to form the radical anion, $TP^{\bullet-}$, which can reduce Co and Fe porphyrins rapidly to the M^0P state. The metalloporphyrins were destroyed during the photochemical process and yet production of CO continued. These findings suggest that catalytic reduction of CO_2 to CO may be affected by the ferrous ions formed after decomposition of the porphyrin ligand. We have found that the mechanism involves different intermediates. The $TP^{\bullet-}$ radical anion reduces Fe(II), and the Fe(I) ions produced react with CO_2 to form an adduct. Subsequent reduction of the Fe-CO_2 adduct by $TP^{\bullet-}$

or by Fe(I) leads to formation of CO. After extensive irradiation, photochemical production of CO stops. This is caused by competition between CO and CO_2 for the Fe(I) binding sites. In all of the above experiments, the catalysts are either destroyed by side reactions or deactivated by attachment of CO. We plan to investigate various strategies to overcome these limitations. A promising route may be the incorporation of the catalysts into solid support, which will protect against undesired side reactions and/or permit recovery and reuse of the catalysts.

Publications:

Dhanasekaran, T., Grodkowski, J., Neta, P., Hambright, P., and Fujita, E. ***"p-Terphenyl Sensitized Photoreduction of CO_2 with Cobalt- and Iron-Porphyrins. Interaction Between CO and Reduced Metalloporphyrins,"*** J. Phys. Chem. A 103, 7742 (1999).

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Grodkowski, J. and Neta, P., ***"Cobalt-Corrin Catalyzed Photoreduction of CO_2,"*** J. Phys. Chem. (in press).

Grodkowski, J. and Neta, P., "***Ferrous Ions as Catalysts for Photochemical Reduction of CO_2 in Homogeneous Solutions,"*** J. Phys. Chem. (in press).

15. *International Standards for Refrigerant Properties*

***M.O. McLinden**, A. Laesecke, E.W. Lemmon, and R.A. Perkins*

Objective: To facilitate and promote international standards for the thermodynamic and transport properties of refrigerants.

Problem: The hydrofluorocarbons (HFCs) and other fluids are now seeing widespread commercial use in place of the ozone-depleting CFC and HCFC refrigerants. To evaluate the energy efficiency, capacity, *etc.*, of any fluid in a thermodynamic cycle, knowledge of the thermophysical properties is required. Standards exist for determining and reporting the performance of air-conditioning systems at standard ratings conditions. But differences between multiple, "competing" property formulations lead to differing performance ratings. This is especially a problem in international trade.

Approach: We work with several international groups that develop and/or promulgate standards. Chief among these is Annex 18 of the International Energy Agency, a group that NIST organized in 1990. We are also active in the Transport Properties Subcommittee of IUPAC. Finally, the NIST REFPROP database has, itself, been adopted as a *de facto* standard within the refrigeration industry. We work within the IEA and IUPAC groups to promote REFPROP as the source of refrigerant property data. As new standards are adopted, we revise REFPROP, if needed, to conform to the new standards.

Results and Future Plans: The IEA Annex 18, Thermophysical Properties of the Environmentally Acceptable Refrigerants, concluded its third and final phase in 1999. The Annex carried out comprehensive evaluations of the available equations of state and sanctioned standards for R123, R134a, R32, R125, and R143a. Wide participation was invited in this process, and anyone could submit an equation of state for evaluation. Of the five fluids, the formulations for R123 and R143a developed at NIST were designated as international standards. A similar comparison of mixture models has facilitated the dissemination and adoption of a new mixture modeling approach. This model, based on Helmholtz energies for each of the mixture components and developed at the University of Idaho and NIST, is implemented in REFPROP and also forms the basis for an extensive tabulation of properties prepared by the Japan Society of Refrigerating and Air Conditioning Engineers. The final report for Annex 18 was presented at the quadrennial Congress of the International Institute of Refrigeration.

Under the auspices of the IUPAC Subcommittee on Transport Properties, NIST acts as one of three coordinators of a project on "Thermochemical, Thermodynamic and Transport Properties of Halogenated Organic Compounds and Mixtures." In the past NIST has organized, through IUPAC, an international round robin comparison of the viscosity and thermal conductivity of R134a. We are now working to develop formulations for propane, butane,

and isobutane (so-called "natural refrigerants") that are of increasing interest.

The ISO has recently approved the establishment of a working group to establish standards for refrigerant properties. NIST will be active in this group, along with many of the Annex participants.

Publications:
McLinden, M.O. and Watanabe, K., ***"International Collaboration on the Thermophysical Properties of Alternative Refrigerants: Results of IEA Annex 18,"*** Proc. 20th Int. Congress of Refrig., Sydney, Australia, September 19-24, 1999, Int. Inst. Refrig.

Lemmon, E.W. and Jacobsen, R.T., ***"An International Standard Formulation for the Thermodynamic Properties of 1,1,1-Trifluoroethane (HFC-143a) for Temperatures from 161 to 500 K and Pressures to 60 MPa,"*** J. Phys. Chem. Ref. Data (in press)

16. *Thermophysical Properties of Natural Gas Systems*

R.A. Perkins, *E.W. Lemmon, T.J. Bruno, D.G. Friend, A.H. Harvey, C.D. Holcomb, M.L. Huber, A. Laesecke, J.W. Magee, M.O. McLinden, S.L. Outcalt, J.C. Rainwater, J.L. Scott, W.M. Haynes, I.M. Abdulagatov (Dagestan Scientific Center), and S. Kiselev (Inst. Oil and Gas Res., Russia)*

Objective: To measure accurately the thermophysical properties of natural gas mixtures and develop standard reference models that are internationally accepted for calculating properties within the required uncertainties of the data over large ranges of temperature, pressure, and composition.

Problem: The thermophysical properties of natural gas systems must be accurately known for national and international custody transfer. It is not possible to measure all possible compositions of natural gas; thus, accurate predictive models are required by industry. These models must be validated with reliable data obtained on a limited number of samples that have well defined compositions. The nature of custody transfer in gas pipelines and liquefied natural gas shipping requires that these models be recognized as national and international standards. Custody transfer also requires that the gas satisfies certain quality (low concentrations of hydrogen sulfide) and odorant safety standards.

Approach: The natural gas systems selected for experimental study are determined by comparisons of the best available models with existing data for systems that are of interest to industry. These comparisons identify systems where additional data are required to fill significant data gaps or where unresolved discrepancies exist between several data sets. Improved Helmholtz energy formulations, which also allow calculation of all thermodynamic properties in the fluid phases of a mixture system in a consistent manner, offer potential for reduced uncertainty for a wider range of mixture systems. Experimental data obtained at NIST on gravimetrically prepared mixtures will extend and enhance the data available in the literature to develop accurate mixture models and to validate the performance of new mixture models. NIST has also been measuring the diffusion coefficient of odorant compounds in gas mixtures in an effort to understand the problem of odorant fading. NIST is currently making measurements of the kinetics and catalysis of the hydrolysis reaction of carbonyl sulfide in propane. This hydrolysis can generate unacceptable levels of hydrogen sulfide in natural gas during transmission.

Results and Future Plans: The Gas Processors Association funded a five-year project to study high pressure gas separation and conditioning which will include phase equilibrium, co-existing density, surface tension, and viscosity measurements and model development. PVT measurements were completed on three mixtures of CO_2 + ethane at temperatures from 200 K to 400 K with pressures to 35 MPa. A paper describing the PVT and isochoric heat capacity measurements on two mixtures of propane and isobutane is in press. Measurements have been completed on the thermal conductivity of propane at temperatures from 83 K to 600 K with pressures to 70 MPa. Although the data are in very good agreement with several reliable researchers, deviations between the best available model and these data reach 10 % at high temperatures. Measurements have been completed on the viscosity of propane and isobutane at temperatures from 300 K to 420 K with pressures to 70 MPa. An improved correlation was published in the Journal of Chemical and Engineering Data in collaboration with IUPAC on the viscosity of propane. These measurements enable improved corresponding states predictions (propane reference fluid) of natural gas

mixture viscosity and thermal conductivity. Measurements are in progress on the thermal conductivity of isobutane and the viscosity of normal butane. A mixture model, based on a generalized corresponding-states algorithm for the excess Helmholtz energy and reference quality formulations for the constituents, has been developed. Long-term plans involve the addition of other fluids such as the heavier hydrocarbons, helium, hydrogen, water, carbon monoxide, and hydrogen sulfide. Modeling work this year has focused on addition of helium, hydrogen, water, and pentane and higher hydrocarbons. NIST is also evaluating the catalytic effects of wetted materials such as stainless steels and aluminum alloys on the kinetics of the hydrolysis reaction of COS in propane.

17. *Properties for Advanced Hydrogen Technologies*

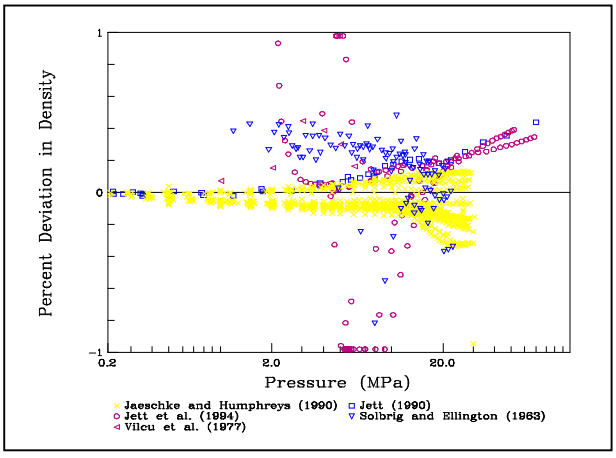
***D.G. Friend**, M.L. Huber, E.W. Lemmon, G.R. Hardin, and J.C. Rainwater*

Objective: To provide industry with high quality thermophysical property surfaces for mixtures of hydrogen and methane over broad ranges of temperature, pressure, and composition.

Problem: There are currently no high accuracy models available that can handle mixtures of hydrogen and methane at high hydrogen concentrations, although fuel cells and hydrogen technologies may play a more important part in satisfying our energy needs. The fuel processing stage in fuel cells, known as reforming, involves processing the fuel to separate hydrogen from the other constituents, and mixtures of hydrogen and methane may be found in this sub-system of a fuel cell. Mixtures of hydrogen and methane have also been proposed as a fuel that may be used directly in internal combustion engines to reduce CO_2 and NOX emissions. The proposed research will develop a model for predicting the thermophysical properties of hydrogen/methane mixtures over the entire composition range from pure hydrogen to pure methane. The topic of this report relates to a project funded by the Electronics and Photonics Technology Office of the ATP program and is part of a more extensive program on fuels and, in particular, on fluids related to natural gas systems. When the cryogenic fluids, hydrogen and helium, are included in such fluids, the standard property formulations must be reconsidered in part because the typical phase envelope topology is 1^C1^Z rather than 1^C as for most other component pairs in natural gas systems.

Approach: Two models which are currently being used to establish standard reference thermodynamic surfaces are the extended corresponding states (ECS) model and a two-fluid Helmholtz mixing model. Both of these can use existing high accuracy pure fluid equations of state for methane and hydrogen, so that the mixture model will reduce to the pure fluid standards in the proper limits. The first step in the project is to perform a literature search and collect and evaluate experimental thermodynamic data (PVT relationships, heat capacities, vapor-liquid equilibria, sound speeds) for the methane/hydrogen binary system. Versions of both the ECS and Helmholtz mixing models were developed to describe the data, and the behavior of the binary interaction parameters was investigated. As the models are developed, comparisons will be made with the experimental database. Upon achieving a satisfactory optimized model, it will be incorporated into a NIST Standard Reference Data mixture database.

Results and Future Plans: There are about 3000 experimental points from 25 sources which give relevant thermodynamic data for the hydrogen-methane system. Although the data situation for the mixture is generally satisfactory, data are sparse for concentrations near the equimolar composition and at the lower temperatures; in addition, there are no caloric data which are generally required to establish the most accurate property standards. Initial results for the ECS model exhibited some numerical convergence problems; thus, much of the development and optimization work has been completed on the two-fluid Helmholtz energy model. Sample



deviations between the data and model are shown in the figure. These results have been implemented in a version of NIST Standard Reference Database 14, although further testing, optimization, and quality control protocols will be required before releasing the revised database.

Future work will concentrate on additional mixtures of natural gas components with hydrogen, *i.e.*, mixtures with ethane, propane, higher alkanes, and multiple components. Although some of the current generation of test vehicles operating on hydrogen-enriched fuels use hydrogen-methane mixtures, the more general fuel will be a mixture of hydrogen and natural gas from an arbitrary source. Results will be incorporated into the NIST property infrastructure as represented by the PC and web-based databases.

18. *Transport Properties of Refrigerants and Refrigerant Mixtures*

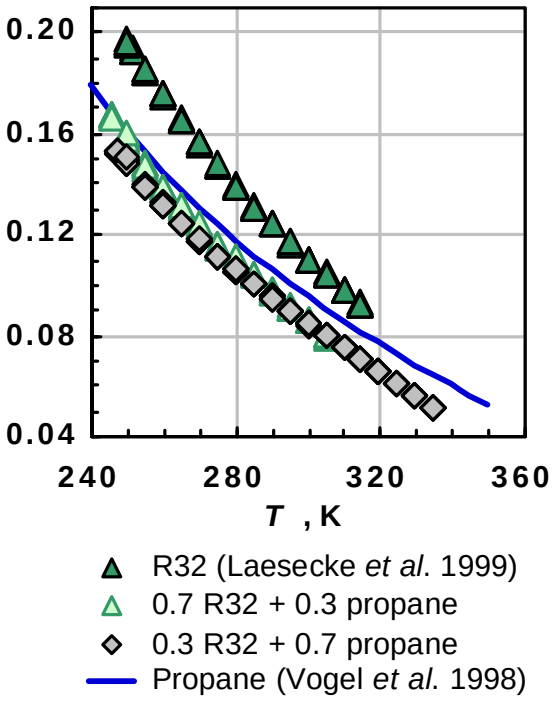
***A. Laesecke**, R.A. Perkins, M.O. McLinden, and M.L. Huber*

Objectives: To resolve large discrepancies between literature data for the transport properties of pure refrigerants and to provide reliable experimental transport properties data for the refrigerant mixtures to develop advanced property models.

Problem: Viscosity measurements for alternative refrigerants, which were carried out in different laboratories since 1988, exhibited differences up to 35%, far in excess of experimental uncertainty. Lack of experimental transport properties data for alternative refrigerant mixtures impedes model refinement and the use of such mixtures in HVAC equipment.

Approach: The NIST sealed gravitational viscometer with a straight vertical capillary was used for new benchmark measurements of saturated liquid ammonia, R32, and R134a to resolve the disconcerting discrepancies between literature viscosity data. Viscosity and thermal conductivity measurements were carried out on four binary and one ternary blend of R32, R125, R134a, and propane (R290), each at two compositions. Measured conditions included subcritical liquid and vapor as well as supercritical phases. Viscosities were measured in the sealed capillary viscometer and in the torsional crystal viscometer. Thermal conductivities were determined from transient and steady-state measurements in hot-wire instruments. These data are used to develop improved transport property models.

Results and Future Plans: Some of the literature data sets did not properly apply necessary corrections in their analysis. Agreement within the combined experimental uncertainty was achieved after applying these corrections. An improved correction for the radial acceleration in viscometers with coiled capillaries was developed. A need was identified to extend international viscometry standards to sealed gravitational capillary instruments. Present standards cover only open capillary viscometers which cannot be used for measurements of volatile liquids. Transfer of sealed viscometer technology to a manufacturer is underway. The mixture measurements revealed strongly non-ideal composition dependences for transport properties in systems of nonpolar/polar compounds such as R32 + propane. The figure shows that the saturated liquid viscosities of both blends are even lower than the viscosity of propane. These results will be incorporated in improved mixture transport property models. The measurements with the torsional crystal viscometer revealed widely varying electrical conductivities and dielectric permittivities of the mixtures.



Non-ideal viscosity of liquid R32 + Propane (R290) mixtures.

Publications:

Kiselev, S.B., Perkins, R.A., and Huber, M.L. ***"Transport Properties of Refrigerants R32, R125, R134a, and R125 + R32 Mixtures in and Beyond the Critical Region,"*** Int. J. Refrig. 22, 509 (1999).

Laesecke, A., Lüddecke, T.O.D., Hafer, R.F., and Morris. D.J., ***"Viscosity Measurements of Ammonia, R32, and R134a. Vapor Buoyancy and Radial Acceleration in Capillary Viscometers,"*** Int. J. Thermophys. 20, 401 (1999).

19. *Radiation Induced Degradation of PCBs in Various Media*

***P. Neta**, D.L. Poster (839), and M. Chaychian, J. Silverman and M. Al-Sheikhly (Univ. of Maryland)*

Objective: To obtain kinetic and mechanistic information on the radiolytic dechlorination of polychlorinated biphenyls (PCBs) in various media and to develop strategies for detoxification of polluted sites by electron beam irradiation.

Problem: The widespread use of polychlorinated biphenyls in various industrial applications presents a major environmental issue because of the toxicity and long lifetime of these compounds in ambient conditions. The method currently used to destroy most PCB containing materials is incineration. This method, however, suffers from two disadvantages: it incinerates the medium along with the PCB, and it converts some of the PCB into more toxic materials, namely dioxins.

Approach: Radiolytic degradation of PCBs is expected to overcome both of these disadvantages. The PCBs in organic solvents such as transformer oils may be reduced into benign inorganic chloride and practically non-toxic biphenyl, without formation of any dioxins. Such treatment leaves the solvents practically unchanged so that they can be recycled instead of incinerated. This approach may be adapted to removal of PCBs in sediments and soils by combining it with extraction or other treatment methods.

Results and Future Plans: We have examined the radiolytic degradation of several PCBs in water/alcohol mixtures, in micellar aqueous mixtures and in transformer oil. We analyzed the various intermediate and final products, investigated the mechanism of reduction, and determined the rate constants for the relevant reactions by pulse radiolysis. Irradiation of PCBs in oil is not expected to lead to dechlorination by direct reaction of the solvated electrons with the PCB, because the oil contains substantial quantities of other aromatic compounds, which also react with solvated electrons very rapidly. Yet, complete degradation of tetrachlorobiphenyl (PCB 54) in transformer oil was achieved by ionizing radiation (200 kGy for 0.27 mg/g PCB 54). By analyzing samples irradiated with various doses, the gradual degradation of PCB 54 and the successive formation and degradation of trichloro-, dichloro-, and monochlorobiphenyl were demonstrated. The final products were mainly biphenyl and inorganic chloride. The mechanism of reductive degradation in transformer oil was established by pulse radiolysis. Irradiation of the oil leads to production of radical anions from the main aromatic components: biphenyl, fluorene, phenathrene, and pyrene. These radical anions transfer an electron to chlorinated biphenyls relatively rapidly, leading to dechlorination. The rate constants for several such reactions, determined individually in 2-propanol solutions, are found to be in the range of 10^7 to 10^8 L mol^{-1} s^{-1}. Electron transfer between the various polycyclic aromatics is a reversible process for which the equilibrium depends on the reduction potential of each compound. Electron transfer to a chlorinated compound, however, is irreversible because of dechlorination. Thus, the reaction can proceed to complete dechlorination even if the rate constants for dechlorination are relatively low.

Future experiments are aimed at demonstrating complete radiolytic degradation of PCBs in actual oil samples of varying PCB contents and in sediments contaminated with PCBs. Irradiation of solid sediments is expected to have low radiolytic efficiency. Attempts will be made to enhance the efficiency by using aqueous suspensions with various additives and by combining ultrasonic treatment along with the irradiation to enhance the transfer of the PCB into the liquid component, where it will be efficiently dechlorinated.

Publications:

Schmelling, D. C., Poster, D. L., Chaychian, M., Neta, P., Silverman, J., and Al-Sheikhly, M., ***"Degradation of Polychlorinated Biphenyls Induced by Ionizing Radiation in Aqueous Micellar Solutions,"*** Environ. Sci. Technol. 32, 270 (1998).

Chaychian, M., Silverman, J., Al-Sheikhly, M., Poster, D. L., and Neta, P., ***"Ionizing Radiation Induced Degradation of Tetrachlorobiphenyl in Transformer Oil,"*** Environ. Sci. Technol. 33, 2461 (1999).

20. *A Screening Tool for the Environmental Impact of New Fluids*

***F. Louis**, C. Gonzalez, V. L. Orkin, M. J. Kurylo, and R. E. Huie*

Objective: To develop a screening tool, based on quantum mechanics, for the prediction of the environmental impact of new classes of halogenated compounds.

Problem: Experimental studies from this Division have demonstrated that the reactivity of the hydroxyl radical toward halogenated organic compounds is not adequately correlated by simple structure-activity relationships. This was particularly evident when an ether linkage was introduced, where even the order of reactivity could not be predicted. This implied that it would be necessary to measure rate constants for a large number of members of any new class of reactants in order to predict the environmental impact of these possible new solvents, refrigerants, or fire suppressants. It was clear that a new approach was needed.

Approach: The basic idea underlying this project is to establish a level of theory which will predict the reactivity of the hydroxyl radical with a series of simple molecules, at the lowest possible degree of computational difficulty. This level of theory is then applied to more complex molecules and, ultimately, it is applied to the new class of interest. Then it is validated by a limited number of experimental determinations. The reality of the approach is much more complex and multidimensional.

Results and Future Plans: In the initial study, several levels of theory were explored for the reaction of OH with CH_2Br_2. This study included the treatment of tunneling in three different manners. This molecule was chosen both because of the importance of bromine as a fire suppressant and because the relatively large electron system of the molecule makes this reaction a serious test of the various levels of theory. Building on the results of this study, the reactions of OH with the other halogen-substituted methanes, up to bromine, were investigated. From these studies, we chose a level of theory and have been investigating the reactions of OH with several fluoroethanes and the ethers derived from them. These pairs were chosen to represent the extremes of behavior observed experimentally: an increase in reactivity upon addition of the ether linkage; a reduction in reactivity; and a small change in reactivity upon addition of the ether linkage. Theory has been able to reproduce the observed trends, with predictions in absolute reactivity within a factor of three. For bis-(difluoromethyl) ether, we have carried out a more exhaustive theoretical analysis of the reaction surface in order to understand better these reactions in general. At the present, we are further refining this approach, with a particular emphasis on better tunneling corrections and the use of pseudo-potentials. Calculations are being extended up to ethers with several carbons and containing fluorine and one or more bromine atoms. In order to verify these calculations, a sample of 2-bromo-1,1-difluoroethyl methyl ether is being synthesized for us, which we will use for an experimental determination of the rate constant.

Publications:

Orkin, V.L., Villenave, E., Huie, R.E., and Kurylo, M.J., ***"Atmospheric Lifetimes and Global Warming Potentials of Hydrofluoroethers: Reactivity Toward OH, UV Spectra, and IR Absorption Cross Sections,"*** J. Phys. Chem. A (in press).

Louis, F.,Gonzalez, C., Huie, R.E., and Kurylo, M.J., ***"An* Ab Initio *Study of the Reaction of Halomethanes with the Hydroxyl Radical. Part 1: CH_2Br_2,"*** J. Phys Chem. A (in press).

Louis, F., Gonzalez, C., Orkin, V., Huie, R. E., and Kurylo, M. J., ***"An* Ab Initio *Study of the Reaction of Halomethanes with the Hydroxyl Radical. Part 2: CH_2F_2, CF_2FCl, CH_2FBr, CH_2Cl_2, CH_2ClBr, CH_3F, CH_3Cl, and CH_3Br; Reactivities and Infrared Radiative Forcings,"*** J. Phys Chem. A (in press).

21. *Databases for Identification of Chemicals by Gas Chromatography: Natural Gas and Alternative Refrigerant Applications*

T.J. Bruno

Objective: To provide an efficient, fast, and reliable method for identifying a wide variety of chemical compounds in both the laboratory and the field. Initial applications include the heavier components of natural gas (the C_6+ fraction), natural gas treatment materials, and alternative refrigerant fluids.

Problem: The design and operation of many processes involving fluids rely on an accurate chemical analysis of the fluid stream composition. For example, calorific value of natural gas is calculated from a chromatographic analysis of each individual gas stream. Custody transfer of natural gas is therefore based upon a detailed compositional analysis. The most common analysis of natural gas at present considers only the lighter components. This approach introduces significant uncertainty to subsequent calculations based on the gas composition. The inclusion of the heavier fraction into the analysis is a complex problem, because the gas consists of upwards of 400 organic and inorganic constituents. Moreover, the composition varies with season, with source-well long-term history, and with short-term usage and storage history. Thus, a fast, low-cost, and reliable method is required for the efficient commerce and use of this vital natural resource. In the refrigeration industry, the thermal properties of a mixed working fluid is strongly composition dependent. Proper refrigeration machine design and operation therefore depends upon an accurate composition measurement. Not only must the initial filling be at precisely controlled mixture compositions, but also maintenance fillings must be so as well. Because the constituents of mixed working fluids leak at different rates, replenishment maintenance requires an accurate fluid chemical analysis.

Approach: Gas chromatography offers an economical and accurate solution to the problem of natural gas analysis and mixed refrigerant fluid analysis. In addition to being one of the most well understood and economical analytical methods available, it is very amenable to field applications. What is needed is an interactive database that can be incorporated into the control and analysis software of both laboratory and field gas chromatographic instrumentation. We have approached the problem of standardizing and automating these analyses through the measurement of standard chromatographic retention parameters on the most useful stationary phases available, and also on some novel developmental phases. The standard retention parameters that we have measured include net retention volumes, relative retentions, and Kovats retention indices. These parameters are corrected for instrumental variation and are, therefore, reproducible from instrument to instrument. The measurements are performed on a specially modified commercial gas chromatograph that provides highly accurate retention information. The column temperature dependence of each retention parameter is modeled with appropriate equations to allow predictions at all relevant temperatures. These models then form the heart of an interactive database that allows off-line identification of peaks and also the optimization of more complex analyses.

Results and Future Plans: The measurement of all standard retention parameters (at several column temperatures) has been completed for 90 natural gas hydrocarbons, 23 natural gas odorization compounds, and 120 alternative refrigerant fluids on ten useful stationary phases. These stationary phases include the methyl silicones and derivatives, porous polymer and solid adsorbents, and some novel stationary phases that include sol/gel phases and clay phases. Several versions of the databases have been released, and are being used in the gas industry and by regulatory agencies. Next year, we will complete the final versions of the databases, suitable for several computer platforms.

Publications:

Bruno, T.J., Bachmeyer, G.M., and Wertz, K.H., ***"Gas Chromatographic Retention Parameters Database for Refrigerant Composition Management,"*** Int. J. Refrig. 21, 639 (1998).

22. *The NIST Mass Spectral Database: Extending the Evaluation*

***S.E. Stein**, A. Mikaya, Jane Klassen, Zhu Damo (Guest Researcher), D. Tchekhovskoi (Contractor), C.L. Clifton, and W.G. Mallard*

Objective: To provide a fully evaluated mass spectral database with tested and documented search algorithms that will enable the positive identification of unknown organic compounds using gas chromatography/mass spectrometry (GC/MS).

Problem: Modern organic analytical chemistry is critically dependent on instrumental analysis. For qualitative analysis, there is no better tool than the mass spectrometer. Like many other analytical techniques, it is best used with a library of reference spectra. Even with good reference spectra, the data must be processed correctly. Robust algorithms that have been thoroughly tested to eliminate flaws are needed.

Approach: The ongoing work after the release of the NIST mass spectral data base, NIST 98, will add new fully evaluated mass spectra to the database of mass spectra with 129,136 evaluated spectra for 107,886 compounds. New data from laboratory work at NIST, spectra purchased from commercial firms, and contributed spectra are being added. As in prior years, emphasis is being placed on the evaluation of the most important spectra and on improvements of the search software.

Results and Future Plans: The addition of the over 17,000 spectra from the National Institute of Materials and Chemical Research of Japan is an important milestone. These spectra are of the highest quality and are primarily focussed on common compounds. The evaluation has been done using the same techniques established for NIST 98. The data were examined for reasonable neutral losses, for air peaks, for impurities, and for errors in transcription. In every case where a change had to be made, agreement between at least two evaluators was required. The analysis was always conservative; if a given spectrum or spectral feature was not clearly in error, it was not changed. Evaluation is continuing on the spectra obtained from a number of chemical suppliers.

Development of algorithms to aid in the evaluation, as well as to provide users of the NIST software with tools for analyzing spectra from compounds that are not in the database, is ongoing. The software needed for the basic searching has been steadily improved. The new release adds a number of features that make it easier to use the proven NIST algorithms. In addition, the ability to add user-drawn structures and synonyms to the user data has been implemented.

Work is continuing on the addition of retention indices to the database. The retention index is a measure of the time it takes a compound to elute from the gas chromatography column. For many compounds, which might otherwise be confused just using the mass spectrum, the retention index makes it possible for a more definitive positive identification to be made. An example of an important class of compounds for which the retention time data is especially useful is the hydrocarbons, many of which have very similar mass spectra. The first stage of compiling and entering the data has begun. Tools are being developed for both evaluation of the data and for prediction of retention times for compounds for which data are not available.

Publications:

Ausloos, P., Clifton, C., Lias, S.G., Mikaya, A., Sparkman, O.D., Stein, S.E., Tchekhovskoi**,** D., Zaikin, V., and Zhu, D., ***"The Critical Evaluation of a Comprehensive Mass Spectral Library,"*** J. Amer. Mass. Spect. 10, 287 (1999).

Stein, S.E., Fateev, O.V., Tchekhovskoi**,** D., Zaikin, V., and Zhu, D, Mikaya, A., Sparkman, O.D. Ausloos, P., Clifton, C., Lias, S.G., Levitsky, A., and Mallard, W.G., ***"NIST/NIH/EPA Mass Spectral Database—NIST 98,"*** Standard Reference Database No. 1, Software Release Version 1.

23. *Automated Gas Chromatography/ Mass Spectral Decomposition and Analysis: Tools for Automating and Improving the Use of GC/MS Instruments*

***S.E. Stein**, O. Toropov (Contractor), J. Klassen, W.G. Mallard, and J.J. Reed*

Objective: To develop and test algorithms for automatically deconvoluting and analyzing GC/MS data files using a target library of compounds.

Problem: The program has been funded by the Defense Threat Reduction Agency (DTRA) to provide a method for analyzing for chemical weapons

banned under the Chemical Weapons Convention. The software implementing the algorithms must provide full blinding of the analysis process not to compromise the proprietary data of treaty participants. In general, the manual analysis of GC/MS data files for complex mixtures can be time consuming and error prone. The normal method of doing a background subtraction to extract the single component can be essentially impossible in a complex mixture because there is no background. Even in only moderately complex chromatograms, a manual subtraction can produce seriously erroneous results. In addition, the use of retention information to reduce false positives is far more efficient with computer techniques.

Approach: A detailed noise analysis is performed, followed by a deconvolution of each of the peaks in the total-ion gas chromatogram. The resulting components are then compared to reference spectra using a series of algorithms to emulate the degree of confidence that an analyst would have in the deconvoluted peak. The process of extracting the distinct components out of a complex data file breaks down into four parts: noise perception and evaluation, component perception, signal extraction, and compound identification. The noise perception and evaluation step is central to the analysis because the recognition of the difference between a "real" peak caused by a compound eluting from the column and a "false" peak caused by noise depends upon a knowledge of the nature and size of the noise. Once the noise is understood, the individual components are extracted. The extraction of the signal involves examining the overlap of components and removing mass spectral peaks associated with a different component. Ongoing testing involves a number of laboratories both in the United States and abroad where specific chemical agent samples are examined.

Results and Future Plans: The algorithm was tested extensively by using a target library of chemical weapons agents. Over 40,000 data files were examined to ensure that the algorithm does not produce false positives. At the same time, a number of experiments was performed by other laboratories with low concentrations of chemical agents to demonstrate that the algorithm is sensitive enough to detect true positives at analytically useful concentrations. The results of these tests have shown that the algorithms used in the development of the software are robust and capable of automated and blinded analysis. This year, Version 2 of the software was released. This version includes a number of small changes in the algorithm that resulted from the testing effort as well as the inclusion of the ability to process a number of new instrument file formats.

The use of retention indices is central to the further reduction of false positives. The software developed here has been adapted by the Organization for the Prohibition of Chemical Weapons (OPCW) for use in all inspections involving GC/MS instrumentation. Work to improve the ability to predict retention index data for chemical agents from structural information and from physical property data on analogous compounds is ongoing.

Publications:

S.E. Stein, ***"In Integrated Method for Spectrum Extraction and Compound Identification from Gas Chromatography/Mass Spectrometry Data,"*** J. Amer. Mass. Spect. 10, 770 (1999).

24. *Measurements of Surface Tension of Mixtures*

***C.D. Holcomb**, S.L. Outcalt, and M.O. McLinden*

Objective: To extend significantly the accuracy, the temperature range, and the pressure range of surface tension measurements for mixtures by creating a unique phase equilibrium apparatus with the implementation of a non-visual, non-mechanical method of measuring the surface tension with the simultaneous measurement of the coexisting densities.

Problem: There are three major problems that have prevented the accurate measurement of the surface tension of mixtures over wide ranges of temperature and pressure. The first involves the difficulty of the type of method selected. The more difficult and time consuming the measurement method, the greater are the sources of measurement error. Capillary rise, maximum bubble pressure, Wilhelmy plate, Du Noüy ring, pendant drop, and sessile drop methods all require visual measurements of a height, width, and/or depth to determine accurately the surface tension. These methods require a person or camera and software to make the measurement which can introduce human, optical, or round-off errors. The second problem involves mechanical manipulation of the measurement technique. Capil-

lary rise, Wilhelmy plate, and Du Noüy ring methods all require the measurement device to be submerged in the liquid and then withdrawn. Mechanical manipulations reduce the operating pressure of the system and add experimental complexity to the measurement of the surface tension. Finally, all methods of measuring the surface tension require knowledge of the densities of the coexisting liquid and vapor phases. Currently, the densities are either estimated or calculated from equations of state. By not measuring the densities directly, especially for more complex mixtures, uncertainties in the density prediction increase the uncertainty in the surface tension.

Approach: All three of these major problems have been eliminated in our approach which uses the differential-bubble pressure method of measuring surface tension and two vibrating tube densimeters for measuring the coexisting densities. These are incorporated into a dual-recirculation-loop high-pressure phase equilibrium apparatus that operates between 223 K and 423 K. The differential bubble pressure method is a variation of the maximum bubble pressure method that eliminates the need for a visual measurement of the depth of submersion of the dip tube. Two dip tubes of different radii are submerged in the liquid to the same depth. The difference in the maximum bubble pressures of the two dip tubes is related to the surface tension, but the pressure effect determined from the depth of submersion of the tubes is canceled. Second, the method does not require any mechanical manipulations. The tubes are mounted in a fixed position and only require that the liquid level is high enough to cover the ends of the tubes. Finally, vibrating tube densimeters are mounted in the two recirculation loops of the phase equilibrium apparatus and are used to measure the densities of the coexisting phases. This eliminates the need for predictions or an equation of state to estimate the densities. The temperature, pressure, and compositions of the phases are recorded as part of the basic phase equilibrium measurement.

Results and Future Plans: The surface tensions and densities of pure isopentane, n-hexane, three mixtures of R32/125, three mixtures of R143a/125, two mixtures of R245fa + isopentane, two mixtures of R123 + isopentane, and two mixtures of R123 + n-hexane have been measured in this apparatus from 280 K to 340 K at pressures to 3.2 MPa. These measurements were used to develop a Moldover-Rainwater model for the surface tension of mixtures. Preliminary evaluation of the modified prediction method show better agreement with the experimental data for a wider range of fluids than for the original model. Another advantage of the modified prediction method is that it does not depend on an equation of state to calculate the fugacity fraction. A final advantage of the modified prediction method is that a single interaction parameter can be added to the model to increase the accuracy of the prediction and allow for more accurate predictions for a wider range of systems. In the future we will perform measurements on natural gas mixtures, aqueous/solvent mixtures, and lubricants.

25. *Modeling of Molecular Systems: Thermodynamics, Void Volumes, and Solid-Liquid Equilibrium*

***J.C. Rainwater**, P.D. Beale (Univ. of Colorado), and S.G. Gay (Univ. of Colorado)*

Objective: To develop a molecular theory of solid-liquid equilibrium (SLE) for pure molecular fluids and mixtures, including hydrocarbons, refrigerants, and polar fluids, and to develop techniques for modeling molecular systems in supercooled liquid, glassy, and amorphous states.

Problem: The complete description of a pure fluid or mixture requires knowledge of the fluid-solid boundary. Our SLE research to date indicates that molecular shape is important and that theories restricted to spherical molecules need to be generalized to nonspherical molecules. There exist methods to determine the thermodynamic properties of hard-sphere systems in terms of average void volumes and surface areas, which we are extending to elongated molecules.

Approach: For SLE, we have followed the approach of P.A. Monson of the University of Massachusetts. The molecule is modeled as a fused hard sphere assembly, for example, a homonuclear hard dumbbell for nitrogen or a heteronuclear dumbbell for methyl chloride. For the hard-body system, the solid free energy is determined in a computationally intensive manner by the method of Frenkel and Ladd, in which at least ten simulations must be performed. More theoretically, the free energy is calculated by the Lennard Jones-Devonshire cell model, from the free volume of a test molecule in a cage of fixed neighboring molecules on a lattice.

The liquid free energy is obtained by simulation, and the phase boundary is determined by the double-tangent construction. At the end, mean-field attractive forces and dipole and quadrupole moments are added as perturbations. Free volumes and surface areas are monitored, and expressions are derived for the system pressure in terms of average free volumes and surface areas.

Results and Future Plans: After completion of our study of methyl chloride, we turned our attention to a fluctuating cell theory and the relationships between pressure and void properties for two-dimensional hard dumbbells. The fluctuating cell theory differs from the simple cell theory in that the positions of the cage molecules are allowed to fluctuate, and an average free volume is calculated. The fluctuating cell theory was expected to give better agreement with the results of the full Frenkel-Ladd calculation with multiple simulations than does the simple cell theory. We found this to be true for all hard dumbbells except when the bond length is very small, in the limit of a hard disk. In that limit, we recovered the earlier, counterintuitive discovery of Hoover *et al*. that the fluctuating cell theory gives poorer agreement than the simple cell theory. We have compared our earlier exact solution for void volumes in three dimensions of a hard-sphere system with a newly published, independent solution of the same problem by a group from Princeton and Bell Labs. Numerical results from the two solutions have been shown to be identical. An important remaining goal is to calculate free volumes of three-dimensional hard dumbbells semi-analytically, where the spatial dimensions are integrated analytically and the two angular variables are integrated by polynomial quadruture. At present we have a robust algorithm for the semianalytical method, but it is slower than Monte Carlo. However, there are a number of possible ways of making the semianalytic method substantially faster, and these will be pursued. If successful, the method will allow for a fluctuating cell model in three dimensions with applications to plastic crystals and more complex molecules. Our first planned extensions are to triatomics with dipole moments, such as sulfur dioxide, and molecules that can be approximately modeled as three fused spheres, such as dimethyl ether and propane.

26. *Thermophysical Properties of Partially Characterized Systems*

***M.L. Huber**, D.G. Friend, C.D. Holcomb, S.L. Outcalt, and J.R. Elliott (Univ. of Akron)*

Objective: To provide industry with models for the thermophysical properties of partially characterized systems such as petroleum fractions and lubricants.

Problem: One may encounter fluid systems that cannot be easily characterized in terms of known compositions of pure fluids. An example is a petroleum fraction, where often the fraction is characterized by an average boiling point and a density or specific gravity, and the exact composition of the fluid is not known. Another example of a partially characterized system is a lubricant. These systems are typically proprietary mixtures generally characterized by their viscosity and density. Currently there is a lack of models for the thermophysical properties of these types of systems. In the refrigeration industry, the lack of adequate models for mixtures of alternative refrigerants and lubricants prevents optimal equipment design.

Approach: We are pursuing two different approaches that build upon existing work performed at NIST. For petroleum fractions, we are developing models based on the theory of extended corresponding states that has been shown to be reliable for nonpolar hydrocarbons of low-to-moderate molar masses. For synthetic lubricant systems, we are investigating the use of various equations of state such as statistical associating fluid theory (SAFT) and Elliott, Suresh and Donahue (ESD). In addition to these models, we plan to model the mixture with a Helmholtz-energy-based mixture model that has been very successful in modeling the thermophysical properties of refrigerants and refrigerant mixtures. This allows us to build upon and enhance existing NIST databases such as NIST4 (Thermophysical Properties of Hydrocarbon Mixtures) and NIST23 (REFPROP: Thermodynamic Properties of Refrigerants and Refrigerant Mixtures).

Results and Future Plans: We have developed an upgrade to the NIST4 (SUPERTRAPP) database that allows computation of the thermophysical properties of undefined petroleum fractions (only API gravity and an average boiling point are required). The new version is currently undergoing review by Standard Reference Data, and we antici-

pate the public release of this new version in the very near future.

We began our refrigerant/lubricant work with some preliminary bubble-point measurements on the R134a/lubricant system. We applied the ESD equation of state and made comparisons with our own data and with literature data. The results of the work so far are promising, but it is only a first step in the analysis of refrigerant/lubricant systems. As more data become available for the lubricant, we will further develop our models for the lubricant. Future work on the mixture model will focus on developing mixing and combining rules. The eventual goal is to incorporate lubricants into the REFPROP database.

Publications:

Huber, M.L., Holcomb, C.D., Outcalt, S.L., and Elliot, J.R., ***"Vapor-Liquid Equilibria for a R134a/Lubricant Mixture: Measurements and Equation-of-State Modeling,"*** ASHRAE Trans. (in press).

Huber, M.L., ***"NIST Standard Reference Database 4: NIST Thermophysical Properties of Hydrocarbon Mixtures, Version 3.0,"*** National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, MD (1999).

27. *Behavior of Fluid Systems Under Shear: Characterization and Metrology*

C. D. Muzny *and H.J.M. Hanley*

Objective: To understand the relationship between fluid properties and shear and subsequently to control nanoscale structural properties through the application of shear.

Problem: The flow properties of a complex system can be predicted or controlled if the relationship between its structure and rheological characteristics is understood. We argue that the structure can be determined by radiation scattering, but that such data must be correlated with rheological data obtained simultaneously from a rheometer or viscometer.

Approach: We recently modified a constant stress rheometer adapted so that a Couette cell can be placed in the neutron beam. The apparatus is capable of high accuracy measurements with viscosities that can range over about ten orders of magnitude. This apparatus is a powerful, generic contribution to the metrology required to investigate systems out of equilibrium. We have also adapted our light scattering equipment to extract dynamic information from a particular shear-modified gelling sample. The results from all of these experiments are coordinated with computer simulation data of model systems under shear.

Results and Future Plans: Studies with our neutron scattering adapted rheometer include correlating the alignment of macromolecules with their viscosity in solution and extensive investigations relating structure changes with viscometry of gelling colloidal silica. Our light scattering system has recently be used in studies of gelling systems under oscillatory shear, the results of which can lead to a better understanding of the chemistry of the process. Computer simulation results on the morphology and structure factor of a two-dimensional system of particles interacting through a Lennard-Jones potential, modified to include a long-range repulsive component, have also been reported. It was shown that gel formation can be regarded as the competition between the short-range attractive forces (cause aggregation) and the long-range repulsion forces (keep particles separate) that encourage the formation of space-filling networks.

Future plans include extending our investigations to x-ray scattering, and to extend the current small angle neutron and light facilities. If successful, we will then have the potential not only to investigate materials over the wide range of length scales, which is our objective, but also will have the flexibility to investigate systems with the most appropriate scattering tool.

Publications:

Straty, G.C., Muzny, C.D., Butler, B.D., Lin, M.Y., Slawecki, T.M., Glinka, C.J., and Hanley, H.J.M**.,** ***"An in situ Rheometric Shearing Apparatus for SANS,"*** Physica B: Condens. Matter 241-243, 74 (1998).

Butler, B.D., Muzny, C.D., and Hanley, H.J.M., "***Scaling of Small-Angle Neutron Scattering Intensities from Gelling Colloidal Silica***," Int. J. Thermophys. 20, 35 (1999).

Hanley, H.J.M., Muzny, C.D., Butler, B.D., Straty, G.C., Bartlett, J., and Drabarek, E., "***Shear-Induced***

Restructuring of Concentrated Colloidal Silica Gels," J. Phys: Condens. Matter 11, 1369 (1999).

Butler, B.D. and Hanley, H.J.M., ***"Aggregation in Quenched Systems Interacting via a Short-Range Attractive, Long-Range Repulsive Potential,"*** J. Sol. Gel Sci. and Tech. 15, 161 (1999).

Muzny, C.D., Butler, B.D., Hanley, H.J.M., and Agamalian, M.***, "An Ultra-Small-Angle Neutron Scattering Study of the Restructuring of Sheared Silica Gels,"*** J. Phys: Condens. Matter 11, L295 (1999).

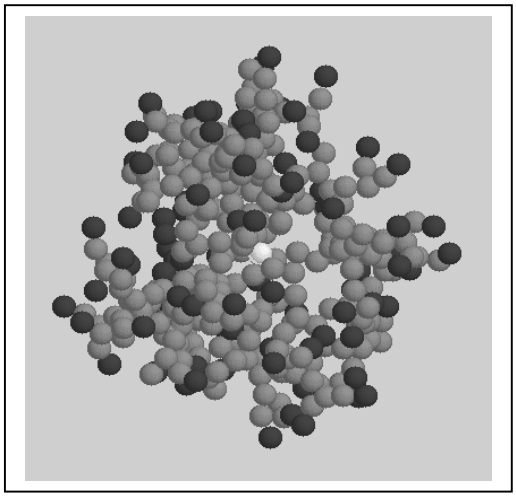
28. *Theory and Simulation of Complex Fluids*

L. Lue*, B.D. Butler, D.J. Evans (Australian Natl. Univ.), L.V. Woodcock (Univ. of Bradford), and S. Gay (Univ. of Colorado)*

Objective: To develop new, more efficient computer simulation methods for complex fluid and solid systems; to improve our understanding of single component and multi-component atomic and molecular models, both in and out of equilibrium; and to improve current predictive models of fluid properties through a better understanding of model systems.

Problem: In general, computer simulation is not effective at predicting, from first principles, the behavior of real fluids with the accuracy required by chemical engineers. This is not only because of current limits on computational resources; the available simulation methods and algorithms also need to be improved. However, by providing an "ideal" laboratory in which to study the behavior of systems containing a large number of interacting particles, computer simulation provides an important tool in the study of the thermophysical properties of complex fluid and solid systems. This "ideal" laboratory allows precise testing of theories for real systems. In addition, computer simulation yields insights into the fundamental nature of the structure and dynamics of complex systems. These insights, for example, have been incorporated into semi-empirical equations that are used for the prediction of fluid properties in technologically important systems. The improvement and application of computer modeling algorithms are thus essential for progress in the development of prediction tools required by industry.

Approach: Our simulation and modeling activities concentrate on areas of current interest in the Division. Some examples include the process of aggregation in quenched systems as models of gelation phenomena, the effects of shear on the thermodynamic states of fluids, steric effects in binary systems and their implications on solid-fluid equilibrium, and the behavior of macromolecules. By identifying and isolating weaknesses in current methods and theories, alternatives are developed, tested, and improved.



Results and Future Plans: Aggregation phenomena have been investigated in systems with potential functions that contain a short-range attractive and long-range repulsive component. These systems reproduce many interesting effects observed in real aggregating systems, such as network formation. A crossover theory for the structure and thermodynamics of linear and star polymers in good solvents has been developed and tested using Monte Carlo methods. This theory is able to describe the scaling behavior of dilute to semidilute polymer solutions, as well as the properties of concentrated polymer systems. Monte Carlo studies have also been performed for dendritic polymer solutions (cf. figure). Methods to study depletion forces that arise from entropic considerations in binary hard-sphere systems have also been developed. The concept of "configurational temperature," which was previously developed and tested for atomic systems, has been extended to molecular systems. A generalization of the Poisson-Boltzmann equation that accounts for nonelectrostatic interactions has been developed. Future plans include the incorporation of the concept of configurational temperature to the thermostatting of nonequilibrium molecular dy-

namics models, the study of shear on aggregation processes, the simulation and modeling of glassy systems, and the testing of theoretical predictions of phase equilibria in binary mixtures.

Publication:
Lue, L. and Kiselev, S.B., ***"Crossover Approach to Scaling Behavior in Dilute Polymer Solutions: Theory and Simulation,"*** J. Chem. Phys. 110, 2684 (1999).

29. *Molecular Dynamics Examination of Microheterogeneity in Liquids*

R. D. Mountain

Objective: To develop models that describe the size of microheterogeneous regions (on molecular length scales) in supercritical fluids and in aqueous mixtures.

Problem: Reactions involving solutes can be significantly influenced by the presence of void regions (supercritical fluids) or by compositional heterogeneities (aqueous mixtures) if the solutes are nonuniformly distributed in the fluid. Knowledge of when and where such nonuniformities occur and how different solutes are partitioned by such environments is lacking and limits our ability to predict and optimize reactions.

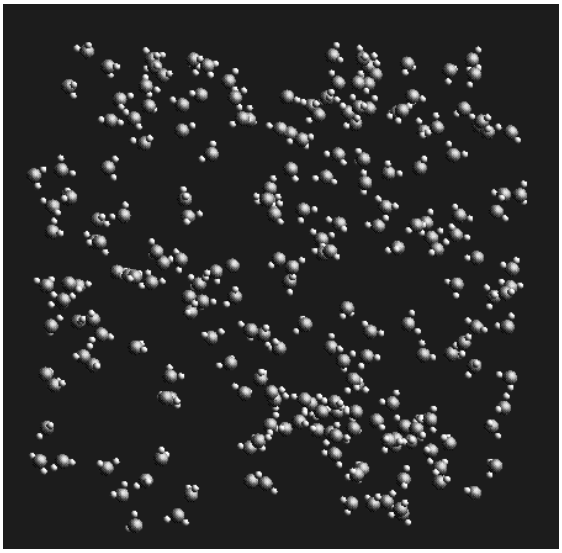
Approach: Molecular dynamics simulations of water, carbon dioxide, acetonitrile, and water-acetonitrile mixtures have demonstrated that existing model potentials for these fluids provide good descriptions of thermal properties. Simulations are being used to determine the size of clusters and voids in supercritical water and in supercritical carbon dioxide. Simulations are also being used to determine the structure of compositional heterogeneities in water-acetonitrile liquid mixtures over a wide range of compostions and temperatures.

Results and Future Plans: Now that the conditions where microheterogeneity occurs for these fluids are known, it is a straightforward task to introduce various solutes into the system.

The simulations are being used to examine the solvation and degree of association of ions in water for ambient and supercritical conditions. Related studies of ions in water-acetonitrile mixtures will be made. Also, the solvation of polar and nonpolar solutes will be examined for the mixtures and for supercritical fluids that relate to experiments underway in the Division.

Publications:
Mountain, R. D., ***"Voids and clusters in expanded water,"*** J. Chem. Phys. 110, 2109 (1999).

Mountain, R. D., ***"Molecular dynamics study of water acetonitrile mixtures,"*** J. Phys. Chem. B (in press)



A snapshot of supercritical water showing the clustering that dominates the structure of the fluid.

30. *Primary Acoustic Thermometry*

D. Ripple *(836), M.R. Moldover, and K.A. Gillis*

Objectives: (1) To reduce the uncertainty in the determination of the thermodynamic temperature by a factor of 3 to 8 in the range from 500 K to 900 K using speed-of-sound measurements in low density argon as a primary standard and (2) to improve the accuracy of the high-temperature fixed points (*e.g.* tin point, zinc point) and radiometry tied to these fixed points.

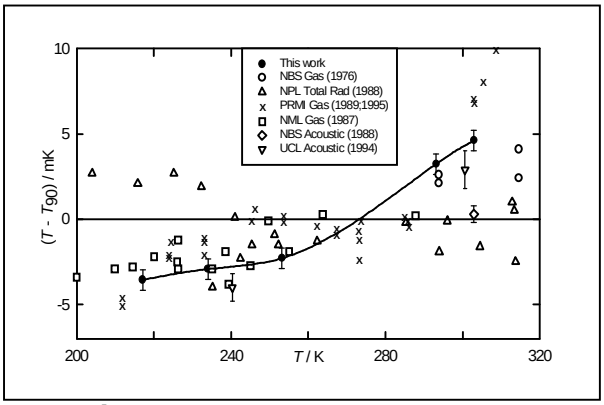
Problem: The most accurate determinations of thermodynamic temperature above 700 K use relative radiance measurements referenced to a black body near 700 K. The thermodynamic temperature of the black body is known from NIST

constant volume gas thermometry (CVGT) experiments. Unfortunately, two NIST CVGT experiments differ from each other for reasons that are not well understood. The difference leads to an estimated uncertainty of 13 mK in temperatures near 700 K and 50 mK in temperatures near the gold point (1337.33 K).

Approach: We measure the frequencies of both acoustic and microwave resonances in a spherical, argon-filled cavity bounded by a thick, metal shell, enclosed by a high-performance thermostat. The data determine the speed of sound in the argon from which the thermodynamic temperature is deduced. The temperature is transferred to platinum resistance thermometers and then to fixed-point devices.

Results and Future Plans: Microwave and acoustic data in the temperature interval 217 K to 303 K were acquired with a prototype resonator. These data determined ($T - T_{90}$), the difference between the Kelvin thermodynamic temperature T and the International Temperature Scale of 1990 (ITS-90) with a standard uncertainty of 0.6 mK, depending mostly upon the model fitted to the acoustic data. The graph compares these data with results from other laboratories.

These results were recognized with the "Best Oral Presentation" Award at the 7th International Symposium on Temperature and Thermal Measurements in Science and Industry. The work with the prototype resonator led to many improvements in the high-temperature apparatus.



During the past year, acoustic resonances were successfully measured at 250 °C, in static argon and also in flowing argon. The latter indicates that the purity of the argon can be maintained at high temperatures. It appears that the performance targets for this apparatus will be met, if not exceeded.

Publication:
Moldover, M.R., Boyes, S.J., Meyer, C.W., and Goodwin, A.R.H., ***"Thermodynamic Temperatures of the Triple Points of Mercury and Gallium and in the Interval 217 K to 303 K,"*** J. Res. Natl. Inst. Stand. Technol. 104, 11(1999).

31. *Advanced Refrigeration Systems for Cryogenic Applications*

***R. Radebaugh**, P.E. Bradley, E.D. Marquardt, M.A. Lewis, and J.D. Siegwarth; I. Ruelich and H. Quack (Technical Univ. of Dresden); M. Hill (Univ. of Colorado); and J. Gary and A. O'Gallagher (891)*

Objective: To use measurement and modeling techniques for evaluating and improving performance of cryocooler components, such as heat exchangers and pulse tubes and to develop new and improved refrigeration and heat transfer processes for the temperature range below about 230 K.

Problem: Cryocoolers are required for many technology areas, including the cooling of infrared sensors for surveillance and atmospheric studies, the cooling of superconducting electronics and magnets, the cooling of cryopumps for clean vacuums in semiconductor fabrication processes, and the liquefaction of natural gas. The use of these technologies has been hampered because of problems with existing cryocoolers. These problems include short lifetimes, inefficiency, high cost, and excessive vibration. Improved cryocoolers would stimulate the growth of all these technology areas. Proper measurements need to be identified that will characterize losses within these cryocoolers, and models need to be developed to optimize the design of such systems.

Approach: Precision moving parts in existing cryocoolers are a source of wear, vibration, and high cost. Our approach in the development of improved refrigeration processes has been to focus our measurements and modeling on processes that eliminate most, or all, moving parts while still maintaining high efficiency. Much of our research has been on pulse tube refrigerators, which have no cold moving parts. Our studies encompass measurements and modeling of losses to further improve

efficiencies of these cryocoolers while increasing their lifetimes. NIST research in this area has much industry and other government agency support to aid in the transfer of this technology to industry.

Results and Future Plans: During FY99, measurements were made on the thermal conductance of packed stainless steel spheres. The thermal conductance degradation factor was found to be 0.11, in good agreement with the value of 0.10 for stainless steel screen. From measurements at various helium filling pressures we have determined that most of the heat is transported by the helium gas a distance of about 4 μm across the boundary rather than by the direct metallic contact. Almost no prior data existed for the thermal conductances of these packed materials, but they are needed for the optimum design of regenerators in many types of cryocoolers. A new *in situ* measurement technique was developed this past year that gave nearly the same result for a regenerator with packed stainless steel screen.

A pulse tube liquefier prototype was completed for NASA/Johnson as part of a program for developing the technology of liquefying oxygen on Mars. NASA expects to have a satellite sent to Mars in the year 2007 that would convert the carbon dioxide atmosphere of Mars into oxygen and then be liquefied using our pulse tube liquefier technology. After two years, a sufficient quantity of liquid oxygen would be collected to fire rockets for lifting off of Mars and returning to Earth with Mars rock samples. Extensive measurements with this liquefier prototype were completed and the results were used to update our models of pulse tube refrigerators. Several types of losses were identified and measured to explain the very high efficiency. The Carnot efficiency of 20 % with respect to input PV power is among the best ever achieved in a cryocooler of this size. This excellent performance indicates the power of the NIST modeling and optimization tools to advance cryocooler technology.

Under sponsorship from the Air Force and the National Radio Astronomy Observatory (NRAO), a program was begun to understand better the thermodynamic and heat transfer processes within regenerators and pulse tubes when operated at high frequencies (< 25 Hz) and temperatures as low as 10 K. Typically, regenerators have had difficulty operating under these conditions and, as a result, have hampered the development of high efficiency and high reliability cryocoolers for temperatures below about 30 K. NRAO and the Air Force have need of such cryocoolers.

32. *Standards for Cryogenic Flow*

***J.L. Scott**, M.A. Lewis, and J.D. Siegwarth*

Objective: To maintain the national standard for cryogenic flow measurement and to advance our services by improving data acquisition, piping configuration, process control, and by reducing measurement uncertainty.

Problem: The cryogenic flow calibration facility is the only independent facility of its kind in the world. It provides the measurement standard for liquefied air gases, and it can be used to evaluate metering methods for liquefied natural gas (LNG), as it becomes a viable alternative fuel. A dynamic weighing system is used to measure the total mass and, with the use of thermophysical property data for density, the volume. Calibrations are typically performed using liquid nitrogen over a flow range of 0.95 kg/s to 9.5 kg/s, a pressure range of 0.4 MPa to 0.76 MPa, and a temperature range of 80 K to 90 K. The precise measurement of any fluid is difficult due to the variability in numerous process conditions; with roughly 570 L of liquid nitrogen at 80 K, the complexity of the measurement is substantially increased. The flow measurement uncertainty is a combination of uncertainties in mass, time, temperature, pressure, and, if volume flow is required, an equation of state for density calculations. While the uncertainty of mass flow measurement is 0.17 %, our uncertainty in volume flow measurement has been three times larger. The new equation of state for nitrogen will make the volume flow measurement uncertainty virtually the same as that of mass flow. Our attention is also focused on mechanical aspects; we must anticipate and prevent component failures due to age and temperature extremes. We want the flow entering the meter under test to be as reproducible as possible, and we must keep the operation and control software on a current platform and in a form that is adaptable to future system operations.

Approach: Improvements are made on a continuing basis to the operation and reliability of the cryogenic flow facility. All components of the weighing system must be in thermal equilibrium with the liquid nitrogen, and, for that reason,

measurements are made dynamically. We have upgraded our load cell, the primary measurement instrument in the process, and acquired a high-speed, high-accuracy digital voltmeter to read it. The result is improved reproducibility. The most difficult process control is temperature control. Almost the entire apparatus is vacuum-jacketed with soldered copper piping. As age and thermal cycling compromise these lines, they are replaced by standard stainless steel vacuum piping with o-ring joints. This makes access and modifications simpler. To minimize the effect of flow disturbances upstream of the test section, we have positioned as much straight pipe upstream of the meter installation, as our laboratory space will allow; however, this enhances the problems of pipe contraction at cryogenic temperatures. The inside lines contract, but the vacuum jacket does not. A robust bracing system and a combination of bellows were designed to compensate for these contractions. In the 1980's a minicomputer was installed for data acquisition of the many sensors throughout the system. Though the best choice at the time, operation was cumbersome and difficult. A PC with a graphical programming language now performs the data acquisition. This not only enhances programming flexibility, but it makes it easier to train additional facility operators. This software incorporates a new equation of state for nitrogen as well as the equation that is currently in NIST 12. The new equation will become the NIST standard when the next version of NIST 12 is released (FY00).

Results and Future Plans: We calibrate and/or test various types of flowmeters (turbine, Coriolis, positive displacement) for customers that include meter manufacturers, state regulatory agencies, and aerospace companies. These meters may be used for transfer standards or in test stands. Our independent cryogenic flow calibration facility can help meter manufacturers compete in the international marketplace by providing interlaboratory comparisons with privately held foreign facilities. Continuing improvements to the facility include reducing heat leaks, expanding the flow range of the facility, enhancing automation, and evaluating our processes to ensure that the national cryogenic flow standard is state of the art.